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CONTRIBUTION TO THE STUDY OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

IV.—IODIDES, CYANIDES, NITRATES, AND SULPHATES.[1]

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The large number of investigations which have had to do with the problem of the condition of double salts in solution have been discussed briefly by Jones and Mackay.[2] It remains to consider here the work which has been done since their paper appeared.

Double salts in general have been divided into two classes by Ostwald,[3] who distinguishes between what he terms "complex salts" and "double salts." The former include those molecular complexes which are capable of existing as such in aqueous solution—not undergoing decomposition into their constituent salts. These dissociate into a cation consisting of the more positive metal, and an anion consisting of the acid complex. For example, potassium ferrocyanide is dissociated in water into :

$$\overset{+}{K} + \overset{+}{K} + \overset{+}{K} + \overset{+}{K} + Fe(\overset{\equiv}{CN})_6.$$

[1] From the dissertation of B. P. Caldwell, submitted to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy, January, 1901.

[2] This JOURNAL, 19, 83.

[3] Ztschr. phys. Chem., 3, 599.

"Double salts" are supposed to break down at once in water into their constituents, and are formed only at the instant when the double salt crystallizes out from the solution.

There are, however, all gradations between "complex" and "double salts." Many "double salts," although largely decomposed by water into their constituents, are still capable of existing to some extent in concentrated solutions.

A special study has been made in this laboratory of the conductivity of double salts, which would not ordinarily be classed among the complex salts. Jones and Mackay[1] studied certain alums and found that the difference between the conductivity of the alums and the sum of the conductivities of the constituent salts was greater than that which exists between the conductivity of mixtures of salts not capable of forming double salts, and the sum of their separate conductivities. They concluded that the alums studied are to be classed as true double salts, even while in solution. At very great dilution, however, no distinction could be drawn between their behavior and that of a mixture of the constituents.

Somewhat later Jones and Ota[2] extended the work to certain double chlorides and obtained, in general, the same results. It was evident, however, that the solution assumes the condition of a mixture of the constituent salts at much smaller dilution, that is, the complex ion breaks down into simpler ones much more easily under the influence of increasing dilution than in the double sulphates. Jones and Knight[3] continued the work and investigated the behavior of certain other double chlorides and double bromides. As the work here described is an extension of the above to certain double sulphates (not alums), iodides, cyanides, and nitrates, and as the same method of work was adopted, it need not be more fully discussed here.

Reasoning from Arrhenius' theory of isohydric solutions MacGregor[4] has deduced certain methods for calculating the conductivity (and other properties of the ions), of mixtures of

[1] This JOURNAL, **19**, 83.

[2] *Ibid.*, **22**, 5.

[3] *Ibid.*, **22**, 110.

[4] Phil. Mag., [5], **41**, 276 (1896); Trans. N. S. Inst. Sci., **9**, 101; Trans. Roy. Soc. Can., (2) **2**, sec. 3, 65.

electrolytes which do not act upon one another chemically. These were based upon the quantities of the single constituents present in a given volume of the solution, the amounts of their dissociation, and their molecular conductivities at infinite dilution.

If v is the volume of a solution which contains n_1, n_2, n_3, ..., etc., gram equivalents of the respective electrolytes present; if α_1, α_2, α_3, ..., etc., are their respective coefficients of dissociation or ionization, and if μ_{α_1}, μ_{α_2}, μ_{α_3}, ... etc., are their respective specific conductivities per gram-equivalent at infinite dilution, then, according to the above theory, the specific conductivity of the solution is equal to :

$$\frac{1}{v}(\alpha_1 n_1 \mu_{\alpha_1} + \alpha_2 n_2 \mu_{\alpha_2} + \alpha_3 n_3 \mu_{\alpha_3} + \text{.... etc.}).$$

He then deduces four equations which, if graphically employed, enable one to calculate the conductivity of mixtures of electrolytes to a high degree of accuracy in dilute solutions. In a mixture of electrolytes each may be considered as occupying its own distinct portion of the solution. If we denote the electrolytes by 1 and 2, the concentrations (in gram-equivalents per liter) of the solution with respect to them by n_1 and n_2, respectively, their ionization coefficients by α_1 and α_2, and their regional dilutions (in liters per gram-equivalents) by v_1 and v_2, respectively, then, when the solutions are in equilibrium with respect to each other,

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2} \quad \text{..... (1)},$$

that is, the numbers of the free gram-ions of the electrolytes per unit volume of their respective regions are equal;

$$n_1 v_1 + n_2 v_2 = 1 \quad \text{..... (2)},$$

that is, the volume of the solution is equal to the sum of the volumes of the regions of the respective electrolytes;

$$\frac{\alpha_1}{v_1} = f_1(v_1) \text{..... (3)},$$

$$\frac{\alpha_2}{v_2} = f_2(v_2) \text{..... (4)},$$

that is, the regional ionic concentrations are functions of the respective regional dilutions.

By means of curves these relations are worked out more easily than by pure mathematics, and the estimation of the conductivity of mixtures at different dilutions can be accurately made. In testing MacGregor's graphical method the work of his students[1] has shown that in dilute solutions it holds accurately, but that in more concentrated solutions, where the μ_a of the constituent salts cannot be considered the same (due to the presence of a large quantity of another salt) as when water alone is the solvent, discrepancies arise.

The large amount of work which has been done thus far on the condition of double salts in solution would seem to justify the following conclusions:

Ostwald's distinction between "complex" and "double salts" holds fairly well in very dilute solutions. In such solutions "double salts" break down completely into their constituents and these dissociate in the usual manner. "Complex salts," on the other hand, do not completely break down into their constituents, even at very great dilutions, although they show a marked tendency to decompose as the dilution of the solution is increased. Those salts which, in dilute solution, have different properties from those of the constituents, give, on electrolysis, a complex anion. Thus, the compound K_2PtCl_6, when electrolyzed, yields the ions $\overset{+}{K} + \overset{+}{K} + \overset{=}{PtCl_6}$. "Double salts," in dilute solution, are completely broken down into their constituents, and, therefore, do not yield any such complex anion when subjected to electrolysis.

It has been pointed out that the distinction between "complex salts" and "double salts" does not hold at all in concentrated solutions. Many so-called double salts exist to a very considerable extent in concentrated solution, as has been shown especially by the work which has been done in this laboratory.

The present investigation was undertaken with the desire of obtaining further knowledge with respect to certain groups of

[1] McIntosh: Trans. N. S. Inst. Sci., 9, 120 (1895-'96); Phil. Mag., (5), 4, 510 (1896); Archibald: Trans. N. S. Inst. Sci., 9, 291, 307, 335; Trans. Roy. Soc., Can., (2), 3, sec. III., 69 (1897-'98). McKay: Trans. N. S. Inst. Sci., 9, 321 (1897-'98).

substances which had already been studied to some extent, and also to acquire information concerning classes of substances about which little or nothing was known. Our work includes a number of double sulphates which are not alums, certain double nitrates and iodides, and a double cyanide. The work consists in comparing the molecular conductivities of the double salts with the sum of the conductivities of their constituents under the same conditions of concentration. Some freezing-point work was also done.

METHOD OF WORK.

The Kohlrausch method of measuring conductivity was employed, a "manganin" wire being used upon the bridge. The induction coil[1] which we used gave such unusual satisfaction that it calls for special comment. By a system of very rigid, thick, steel bars, carrying the make and break spring, an exceptionally high pitch was obtained. The whole was encased in a box, the connections leading to binding-posts on the outside. The adjusting screw was controlled from the exterior. The coil was so noiseless that it could easily have been used on the same desk with the bridge. For convenience it was placed some distance from the bridge.

The resistance coils used were accurate to $\frac{1}{2\,5}$ of 1 per cent.

Two Arrhenius cells were employed in measuring the resistances. The one, with electrodes very wide apart, was used with concentrated solutions, the other with electrodes quite close together, was employed for studying the dilute solutions. The object in using two cells was to be able to throw into the box a considerable resistance for all solutions, and at the same time never be compelled to use such a high resistance that a sharp minimum could not be obtained. The cells were frequently restandardized with a N/50 solution of potassium chloride, and the standardizations were checked by determining for every substance the conductivity of some solution in both cells. All the measuring apparatus used was calibrated by the method of Morse and Blalock.[2]

The double salts were prepared by bringing the constituent salts together in the proper proportions, dissolving the whole,

[1] Made especially to order by M. E. Leeds & Co., Philadelphia.

[2] This JOURNAL, 16, 479.

and evaporating to crystallization. The crystals were freed as completely as possible from the mother-liquor by means of drying paper, and, in every case, analyzed.

The single constituents and double salts were dissolved in pure water, and mother-solutions of convenient strength were prepared and analyzed. From these, suitable dilutions were made. Two methods of diluting were employed. In some cases 50 cc. of the solution were measured into the conductivity cell, and after its conductivity had been determined, 25 cc. were withdrawn by means of a pipette and the same amount of water added in cases where it was wished to double the volume of the solution. In this way dilutions were made in the cell from a solution of volume 1 to volume 2, to volume 4, to volume 8, to volume 20. A solution of volume 20 was then made from the original solution directly in a measuring flask, and its conductivity compared with that of the solution made by successive dilutions in the cell. Very small differences were noted, and the proportional corrections[1] were applied to the solutions previously made. This latter solution was then diluted in the cell three or four times, and the conductivity of the last solution compared with one of the same concentration made directly from the original mother-solution.

The other method of diluting was very simple. It consisted in making each dilution directly from the mother-solution. For example, from a solution of volume 1, solutions of volumes 2, 4, 8, 20, 40 would be prepared in measuring flasks. Further dilutions would then be made from the last (40) as a mother-solution.

It has been argued in favor of the first method that time is saved. We are of the opinion that not only is the second method more accurate but it does not require any more time.

All the water used in making up the solutions and washing out the apparatus was purified by distillation in the manner described by Jones and Mackay.[2] Corrections were applied to the conductivities of the dilute solutions for the conductivity of the water. The conductivity of the water was determined for each substance. The conductivity of the water ranged

[1] Kohlrausch: Wied. Ann., **26**, 184 (1885).

[2] Ztschr. phys. Chem., **22**, 237; This JOURNAL, **19**, 91.

from 1.1×10^{-7} to occasionally 3.0×10^{-7}. All water was preserved in vessels which had been used alone for that purpose for a number of years.

CONDUCTIVITY MEASUREMENTS.

In the work which is discussed below all the solutions were made up on the basis of the molecular weight of the substance. A solution of volume 1 contains 1 gram-molecular weight of the substance in a liter of solution. The symbol v is used to denote the number of liters of the solution which contains 1 gram-molecular weight of the substance. The symbol μ_v is used to denote the molecular conductivity of the solution at the volume v. The column marked "concentration" in the tables contains the strength of the solution in terms of 1 gram-molecule per liter as normal.

Double Iodide of Potassium and Cadmium.

The conductivity of cadmium iodide had been determined by Grotrian and Wershofen,[1] and we have interpolated from their values.

Table I.—Conductivity of Cadmium Iodide.

Cadmium iodide, CdI_2. Molec. wt., 365.70.

v.	$\mu_{v_{18°}}$.	v.	$\mu_{v_{18°}}$.
1	....	40	73.4
2	28.2	100	99.6
4	34.0	200	121.8
10	43.8	400	143.4
20	55.6	1000	171.8
		2000	183.2

The conductivity of potassium iodide had been determined by Kohlrausch,[2] and we have interpolated from his values.

Table II.—Conductivity of Potassium Iodide.

Potassium iodide, KI. Molec. wt., 166.0.

v.	$\mu_{v_{18°}}$.	$2\mu_{v_{18°}}$.	v.	$\mu_{v_{18°}}$.	$2\mu_{v_{18°}}$.
1	96.8	193.6	50	113.2	226.4
2	99.7	199.4	100	116.1	232.2
5	102.4	204.8	200	118.3	236.6
10	106.9	213.8	500	119.7	239.4
20	110.2	220.4	1000	120.3	240.6
			2000	121.2	242.4

[1] Wied. Ann., **18**, 177 (1883); Ztschr. phys. Chem., **5**, 481 (1890).
[2] Wied. Ann., **26**, 161 (1885).

The conductivity of the double iodide of potassium and cadmium had been determined by Grotrian and Wershofen.[1]

Table III.—Conductivity of Potassium Cadmium Iodide.

Potassium cadmium iodide, K_2CdI_4. Molec. wt., 697.70.

v.	$\mu_{v_{18}}$°.	v.	$\mu_{v_{18}}$°.
2	151.6	100	285.4
4	166.0	200	313.0
10	188.0	400	344.8
20	208.0	1000	378.0
40	228.8	2000	401.0
		4000	408.0

The comparison of the conductivity of the double salt with the sum of the conductivities of the constituent salts must be made so as to take into account the fact that 2 molecules of potassium iodide are present in the double salt to every one of the cadmium iodide. Twice the conductivity of the potassium iodide at one-half the dilution of the cadmium iodide is added to the conductivity of the latter, and the sum is compared with that of the double salt at the latter volume.

Table IV.—Comparison. Potassium Cadmium Iodide.

v.	$2\mu_{v_{18}}$°, KI.	v.	$\mu_{v_{18}}$°, CdI_2.	Sum.	$\mu_{v_{18}}$°, K_2CdI_4.	Difference.
1	193.6	2	28.2	221.8	151.6	70.2
2	199.4	4	34.0	233.4	166.0	67.4
5	204.8	10	43.8	248.6	188.0	60.6
10	213.8	20	55.6	269.4	208.0	61.4
20	220.4	40	73.4	293.8	228.8	65.8
50	226.4	100	99.6	326.0	285.4	40.6
100	232.2	200	121.8	354.0	313.0	41.0
200	236.6	400	143.4	380.0	344.8	35.2
500	239.4	1000	171.8	411.2	378.0	33.2
1000	240.6	2000	183.2	423.8	401.0	22.8
2000	242.4	4000	....	....	408.0	....

Double Iodide of Strontium and Cadmium.

This salt was prepared by dissolving together the quantities of pure cadmium iodide and strontium iodide required to make a double salt containing 1 molecule of each constituent. The double salt crystallizes readily, although it is quite soluble. It has the composition $SrCdI_4.8H_2O$.

[1] Wied. Ann., 18, 177; Ztschr. phys. Chem., 5, 481.

Analysis: The cadmium was precipitated from the acidified solution with hydrogen sulphide, and the strontium, after boiling off the hydrogen sulphide, was determined in the filtrate by precipitation with sodium carbonate. The cadmium sulphide was collected in a Gooch crucible and washed with chloroform and carbon bisulphide to remove any precipitated sulphur.

I. 2.2325 grams crystallized salt gave 0.3950 gram CdS and 0.3795 gram $SrCO_3$.

II. 1.9053 grams crystallized salt gave 0.3285 gram $SrCO_3$.

	Calculated for $SrI_2.CdI_2.8H_2O$.	Found. I.	Found. II.
Cd	13.17	13.75	....
Sr	10.17	10.08	10.23

The iodine was determined by titrating the solution with N/10 silver nitrate.

	Calculated.	Found.
I	59.61	59.50

Preparation of the Solution.—The salt was weighed out approximately so as to make a normal solution when dissolved in a liter of water. A portion of the solution was diluted twenty times and titrated against the silver nitrate solution.

The original solution had a concentration 0.9944 normal and its volume was 1.0056.

Table V.—Conductivity of the Double Iodide of Strontium and Cadmium.

Strontium cadmium iodide, $SrCdI_4.8H_2O$. Molec. wt., 846.39.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}}$.
1.0056	0.9944	846.39	91.1
2.0112	0.4972	423.19	121.9
4.0224	0.2486	211.59	144.4
10.056	0.09944	84.639	172.5
20.112	0.04972	42.319	199.9
40.224	0.02486	21.159	235.4
100.56	0.009944	8.4639	289.1
201.12	0.004972	4.2319	324.4
402.24	0.002486	2.1159	357.6
1005.6	0.000994	0.8464	393.2
2011.2	0.000497	0.4232	426.4
4022.4	0.00025	0.2116	454.5
10056.0	0.0001	0.0846	462.6

Table VI.—Conductivity of $SrCdI_4$ Calculated for Even Volumes.

$SrCdI_4$.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	90.93	20	199.82	400	357.6
2	121.58	40	235.05	800	393.2
4	144.17	80	270.84	2000	426.4
8	162.89	200	324.39	4000	454.5

Strontium Iodide.

The salt was purified by crystallization and analyzed.

The solution for the determination of conductivity was made up and standardized by precipitating the strontium as carbonate.

The solution had a concentration of 0.7829 normal, and its volume was 1.2644.

Table VII.—Conductivity of Strontium Iodide.

Strontium iodide, SrI_2. Molec. wt. (cryst.), 449.42.

v.	Concentration.	Grams crystallized salt per liter.	μ_v.
1.2644	0.7829	351.85	150.56
2.5288	0.3914	175.92	169.29
5.0576	0.1957	87.96	181.77
12.644	0.07829	35.18	196.79
25.288	0.03914	17.59	206.04
50.576	0.01957	8.79	217.83
126.44	0.007829	3.518	229.82
252.88	0.003914	1.7592	239.12
505.76	0.001957	0.8796	245.59
1264.4	0.000729	0.3518	248.58
2528.8	0.000391	0.1759	253.89

Table VIII.—Conductivity of SrI_2 Calculated for Even Volumes.

SrI_2.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	146.65	20	202.18	400	242.84
2	161.45	40	212.97	800	247.19
4	176.56	80	222.24	2000	251.78
8	187.59	200	235.40		

The conductivity of cadmium iodide is given above.

Table IX.—Comparison. Strontium Cadmium Iodide.

v.	$\mu_{v_{25}}$. SrI_2.	$\mu_{v_{25}}$. CdI_2.	Sum.	$\mu_{v_{25}}$. $SrCdI_4$.	Difference.
1	146.65	....	....	90.93	....
2	161.45	28.2	189.6	121.58	68.0
4	176.56	34.0	210.56	144.17	66.4
8	187.59	40.6	228.2	162.89	65.3
20	202.18	55.6	257.8	199.82	58.0
40	212.97	73.4	286.4	235.05	51.4
80	222.24	91.0	313.2	270.84	42.4
200	235.40	121.8	357.2	324.29	32.9
400	242.84	143.4	386.2	357.59	28.6
800	247.19	162.4	409.6	381.2	28.4
2000	251.78	183.2	435.0	426.38	8.6

DOUBLE CYANIDE.

Double Cyanide of Potassium and Mercury.

This salt was obtained by crystallization from a solution containing the constituent salts in the proportion to form

$$2KCN.Hg(CN)_2.$$

Analysis.—The mercury was precipitated as mercuric sulphide, and was collected and weighed in a Gooch crucible. The precipitate was washed with carbon bisulphide to remove any sulphur that might have been present. The salt is very hygroscopic, and the crystals taken for analysis were dried on absorbent paper.

I. 1.3529 grams salt gave 0.8025 gram HgS.
II. 1.4593 grams salt gave 0.8641 gram HgS.

	Calculated for $2KCN.Hg(CN)_2$.	Found. I.	II.
Hg	52.33	51.13	51.04

As the substances employed had been previously recrystallized a number of times, and as the crystals of double salt were well formed, and, further, since the substance used for analysis had been only dried on absorbent paper, the analysis was taken to indicate pure double salt, and it was used without further recrystallization for the purpose of the investigation.

The solution prepared for the determination of the electrical conductivity was analyzed in the same way. It was 0.8191 normal, and its volume 1.2210.

Table X.—Conductivity of the Double Cyanide of Potassium and Mercury.

Potassium mercury cyanide, $2KCN.Hg(CN)_2$. Molec. wt., 382.76.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
1.221	0.8191	313.5187	155.0
2.442	0.4095	156.7593	173.1
4.884	0.2047	78.3796	186.8
12.21	0.08191	31.3518	202.0
24.42	0.04095	15.6759	211.5
48.84	0.02047	7.8379	222.0
122.1	0.008191	3.1352	234.0
244.2	0.004095	1.5676	240.0
488.4	0.002047	0.7838	244.3
1221.0	0.000819	0.3135	248.9
2442.0	0.000409	0.1567	251.2
4884.0	0.000204	0.0784	259.5
12210.0	0.000082	0.0313	258.8

Table XI.—Conductivity of $K_2Hg(CN)_4$ Calculated for Even Volumes.

$K_2Hg(CN)_4$.

v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.
2	166.5	40	217.9	800	245.6
4	181.8	80	227.1	2000	250.4
8	193.3	200	237.8		
20	208.1	400	242.8		

Mercuric Cyanide.

The solution was 0.4013 normal, and its volume was 2.4937. The conductivity of this substance is very small, so that only the most concentrated solutions gave distinct readings on the bridge.

Table XII.—Conductivity of Mercuric Cyanide.

$Hg(CN)_2$. Molec. wt., 252.38.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
2.4937	0.4013	101.28	0.2775
4.9874	0.2006	50.64	0.2957
9.9748	0.1003	25.32	0.3198
24.937	0.0401	10.13	0.3787

Table XIII.—Conductivity of Mercuric Cyanide Calculated for Even Volumes.

$Hg(CN)_2$.

v.	$\mu_{v_{25}°}$.
4	0.2884
8	0.3104
20	0.3588

Potassium Cyanide.

The solution used was 1.3944 normal, and its volume 0.7171.

Table XIV.—Conductivity of Potassium Cyanide.

Potassium cyanide, KCN. Molec. wt., 65.19.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}°}$.
0.7171	1.3944	90.9009	110.69
1.4342	0.6972	45.4504	119.74
2.8684	0.3486	22.7252	126.71
7.171	0.1394	9.0900	133.20
14.342	0.0697	4.5450	138.88
28.684	0.0348	2.2725	144.76
71.71	0.0139	0.9090	150.38
143.42	0.0069	0.4545	154.98
286.84	0.0035	0.2272	157.98
717.1	0.0014	0.0909	162.30

Table XV.—Conductivity of Potassium Cyanide Calculated for Even Volumes.

KCN.

v.	$\mu_{v_{25}°}$.	$2\mu_{v_{25}°}$.
1	114.26	228.52
2	122.49	244.98
4	128.41	256.82
10	135.43	270.86
20	141.20	282.40

Since the double salt has the composition $2KCN.Hg(CN)_2$, in making the comparison of its conductivity with the sum of the conductivities of the constituent salts, that of the potassium cyanide must be taken at one-half the dilution and doubled. The case is parallel to that of $2KI.CdI_2$.

Table XVI.—Comparison. Potassium Mercuric Cyanide.

v.	$2\mu_{v_{25}}$ KCN.	v.	$\mu_{v_{25}}$ $Hg(CN)_2$.	Sum.	$\mu_{2v_{25}}$ $K_2Hg(CN)_4$.	Difference.
1	228.52	2	(0.25)	228.77	166.5	62.2
2	244.98	4	0.2884	245.27	181.8	63.4
4	256.82	8	0.3104	257.13	193.3	63.8
10	270.86	20	0.3588	271.22	208.1	63.1
20	282.40	40	(0.39)	282.79	217.9	64.9

The results obtained with the above double iodides and the cyanide show that these salts exist in solution undecomposed into their constituents, in part at least, up to and even beyond a dilution of 2000 liters. The "difference" in the case of the double iodide of potassium and cadmium at a volume of 1 amounts to 31 per cent of the sum of the conductivity of the constituents. In the case of the double iodide of strontium and cadmium it amounts to 35 per cent at a volume 2, and in the case of the double cyanide of potassium and mercury it amounts to 27 per cent at a volume 1.

Jones and Knight[1] found that the "difference" in the case of the double chlorides $2NaCl.ZnCl_2$ and $SrCl_2.2CdCl_2$, amounted to 35.45 per cent for concentrated solution, and that these differences persisted even at a higher dilution than 9000 liters; while in the case of mixtures of chlorides which are not capable of forming double salts, such as $KCl + NH_4Cl$ and $KCl + 2NH_4Cl$, it amounted to only 11 to 14 per cent, and entirely disappeared at about 500 liters.

No very complete information is obtainable as to the behavior of mixtures of iodides. The magnitude of their conductivity is not very different from that of the chlorides, however, and we are justified, by the well-known similarity of the behavior of halogen salts in general, in making the comparison with them. Such a comparison indicates, without doubt, that the iodides under consideration are not completely dissociated in solution. They, also, like the chlorides studied by Jones and Knight,[2] and Jones and Ota,[3] retain their compound character, somewhat, to high dilutions. We are not quite as fully justified in making the comparison of the cyanide with

[1] *Loc. cit.*
[2] *Loc. cit.*
[3] *Loc. cit.*

the chlorides, but, were we to do so, the same conclusion would be reached in regard to them as in the case of the chlorides and iodides.

A comparison with the differences shown by mixtures of bromides which do not combine to form double salts, strengthens the above conclusion. They behave exactly like the chlorides, and there is no reason for supposing that the iodides conduct themselves differently. Direct experimental proof would, however, be desirable.

Croustchoff and Packhoff[1] give some meager information in reference to the behavior of solutions of mixed halides. They find that the conductivity of the solution $\frac{1}{2}(NaBr + KI)$ actually observed is about 1 per cent smaller than that calculated from the conductivities of the constituents. The difference in the case of the solution $\frac{1}{2}(NaI + KBr)$ is given as about 3.5 per cent, while that in the case of $\frac{1}{2}(KI + NaI)$ is about 0.5 per cent.

This is the only direct experimental evidence we possess on the conductivity of mixtures of iodides, and shows clearly the existence of these double iodides in concentrated solution.

DOUBLE NITRATES.

Double Nitrate of Ammonium and Praseodymium.

It was deemed desirable to investigate the condition of double nitrates in solution. Very few double nitrates exist, however, where both constituents are soluble in water. We were fortunate in having at our disposal a fairly good quantity of praseodymium and neodymium nitrates and oxides which were in a high state of purity, having been repeatedly crystallized in the course of an investigation carried on some time ago by one of us[2] on the atomic weights of praseodymium and neodymium.

In the case of praseodymium the substances at our disposal were praseodymium nitrate and the double nitrate of praseodymium and ammonium. The method used for the purification of the materials employed, as well as their degree of purity, are recorded in the article above mentioned.

[1] Compt. rend., 108, 1162.

[2] Jones: This JOURNAL, 20, 345.

Solutions were prepared and standardized by determining the praseodymium. This was precipitated with ammonium hydroxide and the precipitate ignited to oxide in a porcelain boat. This oxide has the formula Pr_4O_7. As there is some doubt as to whether this oxide has a definite composition, the precipitate was ignited in a rapid stream of hydrogen, purified by passing through lead plumbate and silver nitrate; then dried by passing through sulphuric acid, and reduced to the well-known compound Pr_2O_3.

The loss in weight on ignition in hydrogen and the equal gain in weight on subsequent ignition in air convinced us that the oxide Pr_4O_7 does exist, and can be used in the analysis of praseodymium salts.

The concentration of the solution used was 1.2072 normal, and its volume 0.8314.

Table XVII.—Conductivity of the Double Nitrate of Ammonium and Praseodymium.

$2NH_4NO_3.Pr(NO_3)_3$. Molec. wt., 486.82.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
0.8314	1.2027	568.40	134.1
1.6628	0.6013	284.20	248.0
3.3256	0.3006	142.10	334.9
8.314	0.1203	56.84	404.7
16.628	0.0613	28.42	451.1
33.256	0.03006	14.21	491.1
83.14	0.01203	5.684	531.3
166.28	0.006013	2.842	555.8
332.56	0.003006	1.421	580.3
831.8	0.001202	0.5684	613.2
1662.8	0.000601	0.2842	628.0
3325.6	0.000300	0.1421	642.8
8314.0	0.000120	0.0568	654.3

Table XVIII.—The Conductivity of Ammonium Praseodymium Nitrate Calculated for Even Volumes.

$2NH_4NO_3.Pr(NO_3)_3$.

v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.
1	157.0	20	459.2	400	585.0
2	265.6	40	496.5	800	604.0
4	344.3	80	528.8	1000	608.8
8	400.2	100	536.3	2000	631.0
10	413.9	200	560.8	4000	644.3

Praseodymium Nitrate.

This was made from the oxide by treatment with nitric acid and repeated (eight to ten times) evaporation to crystallization to remove all excess of acid.

The solution was standardized in the same manner as the double salt.

The volume of the solution was 2.6305, and its concentration 0.38015.

Table XIX.—Conductivity of Praseodymium Nitrate.

Praseodymium nitrate, $Pr(NO_3)_3$. Molec. wt., 326.58.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
2.6305	0.38015	124.15	153.9
5.2610	0.19007	62.07	186.4
10.5220	0.09503	31.03	213.9
21.0440	0.04751	15.51	239.3
52.610	0.01900	6.207	270.9
105.22	0.00950	3.103	289.7
210.44	0.004751	1.551	308.2
526.1	0.001900	0.6207	336.4
1052.2	0.000950	0.3103	346.5
2104.4	0.000475	0.1551	359.7
5261.0	0.000190	0.06207	374.0
10522.0	0.000095	0.03103	396.0

Table XX.—Conductivity of Praseodymium Nitrate Calculated for Even Volumes.

$Pr(NO_3)_3$.

v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.	v.	$\mu_{v_{25}}$.
2	146.0	40	258.3	800	341.8
4	170.9	80	280.9	1000	345.9
8	200.8	100	288.6	2000	359.3
10	213.9	200	308.4	4000	370.6
20	236.8	400	325.2		

Ammonium Nitrate.

The substance used had been repeatedly crystallized, and dried to constant weight. The solution was then made up by weight.

Table XXI.—Conductivity of Ammonium Nitrate.

Ammonium nitrate, NH_4NO_3. Molec. wt., 80.12.

v.	$\mu_{v_{25}}$°.	$2\mu_{v_{25}}$°.	v.	$\mu_{v_{25}}$°.	$2\mu_{v_{25}}$°.
1	93.87	187.7	50	124.0	248.0
2	101.0	202.0	100	126.8	253.6
4	107.0	214.0	200	129.9	259.8
5	108.2	216.4	400	131.7	262.4
10	114.5	229.0	500	131.8	263.6
20	119.6	239.2	1000	137.2	274.4
40	123.5	247.0	2000	137.8	275.6

In the comparison of the conductivities, since the double salt has the composition $Pr(NO_3)_3.2NH_4NO_3$, we take twice the conductivity of the ammonium nitrate at one-half the dilution.

Table XXII.—Comparison. Ammonium Praseodymium Nitrate.

v.	$2\mu_{v_{25}}$° NH_4NO_3.	v.	$\mu_{v_{25}}$° $Pr(NO_3)_3$.	Sum.	$\mu_{v_{25}}$° Double salt.	Difference.
1	187.7	2	146.0	333.7	265.6	68.1
2	202.0	4	170.9	372.9	344.3	28.6
4	214.0	8	200.8	414.8	400.2	14.6
5	216.4	10	213.9	430.3	413.9	16.4
10	229.0	20	236.8	465.8	459.2	6.6
20	239.2	40	258.3	497.5	496.5	1.0
40	247.0	80	280.9	527.9	528.8	−0.9
50	248.0	100	288.6	536.6	536.3	+0.3
100	253.6	200	308.4	562.0	560.8	+1.2
200	259.8	400	325.2	585.0	585.0	0.0
400	262.4	800	341.8	604.2	604.0	+0.2
500	263.6	1000	345.9	609.5	608.8	+0.7
1000	274.4	2000	359.3	633.7	631.0	+1.3
2000	275.6	4000	370.6	646.2	644.3	+1.9

Double Nitrate of Ammonium and Neodymium.

The neodymium compounds at our disposal were the oxide, Nd_2O_3, and the nitrate, $Nd(NO_3)_3$. As the amount of substance available was not large enough, on account of the tremendous solubility of neodymium salts, to prepare a perfectly dry, double nitrate of neodymium and ammonium by crystallizing from a solution containing the constituents, we made solutions of the constituent nitrates, standardized them, and mixed them in proportions corresponding to the salt $2NH_4NO_3.Nd(NO_3)_3$.

It will be shown later, that such a mixture of salts is not necessarily exactly the same as a solution of the double salt itself, but its manner of ionization is not materially different, and at great dilutions the state of equilibrium is the same in the two cases.

It is obvious that this method of preparing the double salt is open to many objections. The least excess of either constituent will, of course, very materially change the conductivity. And since the equivalency of the quantities of the two solutions mixed is dependent upon the accuracy of both standardizations, the chance for error is comparatively large. We were not surprised, therefore, to find in the comparison of the dilute solutions, as will be seen in the table given below, that the "difference" did not become zero at great dilutions.

The neodymium nitrate was analyzed in the same general way as the praseodymium nitrate. On the addition of ammonium hydroxide a light-pink precipitate of the hydroxide came down. Since neodymium does not form any higher oxide than Nd_2O_3 on ignition in air, the precipitate was not ignited in a stream of hydrogen.

The solution was 0.8445 normal, and its volume 1.1840.

The solution of ammonium nitrate was made up by weight and contained 1 gram-molecule to the liter.

The solution of the double salt was prepared by bringing the constituents together in the proper proportions, and diluting the mixture in a measuring flask to a known volume. The double salt had a volume of 6.

Table XXIII.—Conductivity of the Double Nitrate of Ammonium and Neodymium.

Ammonium neodymium nitrate, $2NH_4NO_3.Nd(NO_3)_3$. Molec. wt., 489.96.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$
6	0.1666	81.66	520.2
10	0.1000	48.996	570.9
20	0.0500	24.498	624.7
40	0.0250	12.249	674.0
80	0.0125	6.129	713.6
100	0.0100	4.8996	733.3
200	0.0050	2.4498	770.2
400	0.0025	1.2249	801.3

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$°.
800	0.00125	0.6129	833.9
1000	0.00100	0.4899	850.2
2000	0.00050	0.2449	877.0
4000	0.00025	0.1224	884.8

Table XXIV.—Conductivity of Neodymium Nitrate.

Neodymium nitrate, $Nd(NO_3)_3$. Molec. wt., 329.72.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$°.
1.184	0.8445	278.45	191.4
2.368	0.4222	139.22	282.0
4.736	0.2111	69.61	344.9
9.472	0.1055	34.80	393.0
23.68	0.0422	13.922	442.0
47.36	0.0211	6.961	475.6
94.72	0.0105	3.480	507.0
236.8	0.0042	1.3922	539.6
473.6	0.0021	0.6961	566.9
947.2	0.0010	0.3480	578.6
2368.0	0.0004	0.1392	599.9
4736.0	0.0002	0.0696	611.4

Table XXV.—The Conductivity of Neodymium Nitrate Reduced to Even Volumes.

$Nd(NO_3)_3$.

v.	$\mu_{v_{25}}$°.	v.	$\mu_{v_{25}}$°.	v.	$\mu_{v_{25}}$°.
1	187.2	20	429.4	400	558.8
2	253.5	40	466.0	800	575.1
4	325.4	80	497.3	1000	579.8
8	378.1	100	510.5	2000	594.5
10	394.8	200	531.2	4000	600.4

The conductivity of ammonium nitrate has been given above.

Table XXVI.—Comparison. Ammonium Neodymium Nitrate.

v.	$2\mu_{v_{25}}$°. NH_4NO_3.	v.	$\mu_{v_{25}}$°. $Nd(NO_3)_3$.	Sum.	$\mu_{v_{25}}$°. Double salt.	Difference.
5	216.4	10	394.8	611.2	570.9	40.3
10	229.0	20	429.4	658.4	624.7	33.7
20	239.2	40	466.0	705.2	674.0	31.7
40	247.0	80	497.3	744.3	713.6	30.7
50	248.0	100	510.5	758.5	733.3	25.2
100	253.6	200	531.2	784.8	770.2	14.6
200	259.8	400	558.8	818.6	801.3	17.3
400	262.4	800	575.1	837.5	833.9	3.8
500	263.6	1000	579.8	843.4	850.2	—6.8
1000	274.4	2000	594.5	868.9	877.0	—6.1
2000	275.6	4000	600.4	876.0	884.8	—8.8

It seems remarkable that the nitrates of two elements so closely related to each other as praseodymium and neodymium should possess such different electrical conductivities. That of neodymium nitrate is nearly 30 per cent larger than that of praseodymium nitrate. These salts are both exceedingly soluble in water and hygroscopic. Attention is called here, and, in a later portion of this paper, will be again called to the fact that, although the determination of the molecular lowering of the freezing-point of water by these substances does not increase regularly with increasing dilution, but shows a reentrant bend in the curve, nevertheless, the molecular conductivity increases regularly. The results show that ammonium praseodymium nitrate dissociates into its constituent molecules completely at about N/20 concentration, and thereafter behaves like a mixture of the constituent salts. The point of complete decomposition in the case of ammonium neodymium nitrate is at a volume of about 500.

Making use again of the data of Croustchoff and Peckhoff[1] for the conductivity of mixtures of electrolytes which do not form double salts, we find it recorded that the difference between the observed conductivity of the mixture and that calculated from the constituents amounts, in the case of the solution $\frac{1}{2}(KNO_3 + \frac{1}{2}Sr(NO_3)_2)$, to less than 1 per cent. The difference found in the results recorded here for ammonium praseodymium nitrate is 20 per cent for a volume 1, and for ammonium neodymium nitrate 10 per cent of the sum of the conductivities of the constituents.

There is, then, no doubt as to the existence of these nitrates at least partially undecomposed in concentrated solution. They soon dissociate into their constituents, however, and conduct themselves like mixtures of the single salts.

DOUBLE SULPHATES.

Double Sulphate of Ammonium and Magnesium.

The double salt was prepared by crystallization from a solution containing the constituent salts in equivalent proportions. The crystals were dried on absorbent paper and analyzed.

In the analysis of both the crystals and the solution of the

[1] *Loc. cit.*

double salt the magnesium was determined by precipitation with disodium phosphate.

Analysis of the crystallized double salt :

	Calculated for $MgSO_4.(NH_4)_2SO_4.6H_2O$.	Found.
Mg	6.75	6.77

The strength of the solution used was 0.6215 normal, and its volume 1.6090.

Table XXVII.—Conductivity of the Double Sulphate of Ammonium and Magnesium.

Ammonium magnesium sulphate. Molec. wt., cryst., 360.76.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}°}$.
1.609	0.6215	224.21	145.0
3.218	0.3107	162.10	187.7
6.436	0.1553	56.05	225.4
16.09	0.06215	22.42	265.5
32.18	0.03107	11.21	298.5
64.36	0.01553	5.605	333.4
160.9	0.006215	2.242	380.0
321.80	0.003107	1.121	409.4
643.60	0.001553	0.5605	443.9
1609.0	0.000621	0.2242	466.6
3218.0	0.000310	0.1121	494.3
6436.0	0.000155	0.0560	509.7

Table XXVIII.—The Conductivity of the Double Sulphate of Ammonium and Magnesium Calculated for Even Volumes.

$(NH_4)_2(SO_4).MgSO_4$.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	128.9	20	273.5	400	417.8
2	155.4	40	306.9	800	447.5
4	196.9	80	340.9	2000	473.3
8	231.9	200	387.1		

The conductivity of magnesium sulphate has been determined by a number of experimenters—by Kohlrausch[1] and Krannhals[2] at 18°, and Walden[3] at 25°. The following values are taken from the work of these experimenters and are probably

[1] Wied. Ann., **26**, 161 (1885).
[2] Ztschr. phys. Chem., **5**, 250 (1890).
[3] *Ibid.*, **1**, 529 (1887).

quite accurate. The three sets of values did not differ very materially from one another when difference in temperature is taken into account.

Table XXIX.—Conductivity of Magnesium Sulphate.

Magnesium sulphate, $MgSO_4$. Molec. wt., 120.42.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
2	62.6	80	139.3
4	76.7	200	165.9
8	89.1	400	184.3
20	110.0	800	199.5
40	123.4	2000	217.5

Ammonium Sulphate.

The material employed was carefully purified by repeated crystallizations.

The strength of the solution used was 0.1426 normal, and its volume 0.8751.

Table XXX.—Conductivity of Ammonium Sulphate.

Ammonium sulphate, $(NH_4)_2SO_4$. Molec. wt., 132.22.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}°}$.
0.8751	1.1426	151.07	124.7
1.75	0.5713	75.53	143.6
3.50	0.2856	37.76	161.2
8.751	0.11426	15.107	182.2
17.50	0.05713	7.553	198.5
35.0	0.02856	3.776	215.0
87.51	0.011426	1.5107	235.3
175.0	0.005713	0.7553	248.3
350.0	0.002856	0.3776	260.9
875.1	0.001142	0.1510	269.5
1750.0	0.000571	0.0755	275.1

Table XXXI.—Conductivity of Ammonium Sulphate Calculated for Even Volumes.

$(NH_4)_2SO_4$.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	127.4	20	199.9	400	261.7
2	146.1	40	216.9	800	268.3
4	163.2	80	232.4	2000	276.6
8	179.2	200	250.1		

Table XXXII.—Comparison. Ammonium Magnesium Sulphate.

v.	$\mu_{v_{25}}$. $MgSO_4$.	$\mu_{v_{25}}$. $(NH_4)_2SO_4$.	Sum.	$\mu_{v_{25}}$. Double salt.	Difference.
2	62.6	146.1	208.7	155.4	53.3
4	76.7	163.2	239.9	196.9	43.0
8	89.1	179.2	268.3	231.9	36.4
20	110.0	199.9	309.9	273.5	36.4
40	123.4	216.9	340.3	306.9	33.4
80	139.3	232.4	371.7	340.9	30.8
200	165.9	250.1	416.0	387.1	28.9
400	184.3	261.7	456.0	417.8	28.2
800	199.5	268.3	467.8	447.5	20.3
2000	217.5	276.6	494.1	473.3	20.8

Double Sulphate of Ammonium and Copper.

The double salt was prepared in the usual way, and crystallizes easily from the solution with 6 molecules of water of crystallization. The crystallized salt was dried on absorbent paper and analyzed.

Analysis $(NH_4)_2SO_4.CuSO_4.6H_2O$:

The copper was precipitated with alkali and weighed as oxide. The sulphuric acid was determined as barium sulphate.

	Calculated.	Found.
Cu	19.90	19.81
SO_4	48.04	47.78

The solution used was 0.5516 normal, and its volume 1.8128. 226.60 cc. of this solution were then diluted to 250 cc. to bring it to volume 2, and the dilutions were made from this as a mother-solution.

Table XXXIII.—Conductivity of the Double Sulphate of Ammonium and Copper.

Ammonium copper sulphate, $(NH_4)_2SO_4.CuSO_4$. Molec. wt., cryst., 400.0.

v.	Concentration.	Grams crystalized salt per liter.	$\mu_{v_{25}}$.
2	0.50	200.00	161.6
4	0.25	100.00	196.6
8	0.125	50.00	226.0
20	0.050	20.00	267.3
40	0.025	10.00	296.8

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}°}$.
80	0.0125	5.00	331.0
200	0.0050	2.00	377.3
400	0.0025	1.00	406.9
800	0.00125	0.50	434.1
2000	0.00050	0.20	470.0

Copper Sulphate.

Kohlrausch[1] determined the conductivity of copper sulphate at 18°. We have used his results, changing them to values at 25° by means of the temperature coefficient 2.25, and have interpolated wherever necessary.

Table XXXIV.—Conductivity of Copper Sulphate.

Copper sulphate, $CuSO_4$. Molec. wt., 159.66.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	43.4	20	98.1	400	174.2
2	55.8	40	109.8	800	192.3
4	66.6	80	128.4	2000	219.8
8	74.5	200	156.2		

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of ammonium copper sulphate with the sum of the conductivities of its single constituents is made below:

Table XXXV.—Comparison. Ammonium Copper Sulphate.

v.	$\mu_{v_{25}°}$. $(NH_4)_2SO_4$.	$\mu_{v_{25}°}$. $CuSO_4$.	Sum.	$\mu_{v_{25}°}$. Double salt.	Difference.
1	127.4	43.4	170.8		
2	146.1	55.8	201.9	161.6	40.3
4	163.2	66.6	229.8	194.6	35.2
8	179.2	74.5	253.7	220.0	33.7
20	199.9	98.1	298.0	266.8	32.2
40	216.9	109.8	326.7	296.8	29.9
80	232.4	128.4	360.8	330.8	30.0
200	250.1	156.2	406.3	377.3	29.0
400	261.7	174.2	435.9	406.9	29.0
800	268.3	192.3	460.6	434.1	26.5
2000	276.6	219.8	496.4	470.0	26.4

[1] Wied. Ann., **26**, 161 (1885).

Ammonium Ferrous Sulphate.

The substance used was the so-called "chemically pure" ammonium ferrous sulphate. It was found that the solution decomposed so quickly at 25° that the conductivity of only four dilutions was measured.

The solution was made up by weighing out the substance so as to have a concentration 0.5 normal. It was also standardized by precipitation with barium chloride.

The mother-solution had a volume 2.0003.

Table XXXVI.—Conductivity of Ammonium Ferrous Sulphate.

Ammonium ferrous sulphate, $(NH_4)_2SO_4.FeSO_4.6H_2O$. Molec. wt., cryst., 392.40.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}}$°.
2	0.5	196.20	156.6
20	0.05	19.62	261.9
200	0.005	1.962	361.8
2000	0.0005	0.1962	466.5

The solution oxidized in the course of the measurements so that the results are not to be regarded as very accurate.

Ferrous Sulphate.

The ferrous sulphate used was made by dissolving an excess of iron (piano wire) in sulphuric acid. An excess of metal was present, while the solution was being concentrated. The substance was analyzed by precipitating the sulphuric acid.

The solution was 0.4664 normal, and its volume 2.1440.

Table XXXVII.—Conductivity of Ferrous Sulphate.

Ferrous sulphate, $FeSO_4$. Molec. wt., 152.06.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$°.
2.144	0.4664	70.92	59.8
21.44	0.0466	7.092	104.5
214.4	0.0046	0.7092	171.0
2144.	0.0004	0.07092	233.0

Table XXXVIII.—Conductivity of Ferrous Sulphate Calculated for Even Volumes.

$FeSO_4$.

v.	$\mu_{v_{25}}$°.	v.	$\mu_{v_{25}}$.
2	59.4	200	170.6
20	104.0	2000	232.0

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of ammonium ferrous sulphate with the sum of the conductivities of its constituents is given below:

Table XXXIX.—Comparison. Ammonium Ferrous Sulphate.

v.	$\mu_{v_{25}}$°. $(NH_4)_2SO_4$.	$\mu_{v_{25}}$°. $FeSO_4$.	Sum.	$\mu_{v_{25}}$°. Double salt.	Difference.
2	146.1	59.4	205.5	156.6	48.9
20	199.9	104.0	303.9	261.9	42.9
200	250.1	170.6	420.7	361.8	58.9
2000	276.6	232.0	508.6	466.5	42.1

Double Sulphate of Ammonium and Cadmium.

The salt was prepared as usual, by crystallizing it from a solution of its constituents.

The crystallized salt, $(NH_4)_2SO_4.CdSO_4.6H_2O$, was dried on absorbent paper and analyzed. The cadmium was precipitated as carbonate and weighed as oxide in a Gooch crucible. The sulphuric acid was determined in the usual way.

Analysis of crystallized salt:

	Calculated for $(NH_4)_2SO_4.CdSO_4.6H_2O$.	Found. I.	Found. II.
Cd	24.97	24.71	24.40
SO_4	42.84	42.80	42.76

The solution was 0.9888 normal, and its volume 1.0113. We then diluted 101.13 cc. to 200 to bring it to a volume of 2, and used this as a mother-solution in subsequent dilutions.

Table XL.—Conductivity of the Double Sulphate of Ammonium and Cadmium.

Ammonium cadmium sulphate, $(NH_4)_2SO_4.CdSO_4$. Molec. wt., cryst., 448.40.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}°}$.
2	0.50	224.20	151.6
4	0.25	112.10	185.0
8	0.125	56.05	216.0
20	0.050	22.42	254.4
40	0.025	11.21	285.5
80	0.0125	5.605	320.6
200	0.0050	2.242	366.2
400	0.0025	1.121	398.4
800	0.00125	0.5605	432.2
2000	0.00050	0.2242	474.0

Cadmium Sulphate.

The solution used was 1.3343 normal, and its volume 0.7496.

Table XLI.—Conductivity of Cadmium Sulphate.

Cadmium sulphate, $CdSO_4$. Molec. wt., 208.06.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}°}$.
0.75	1.3343	277.61	32.5
1.50	0.6671	138.80	45.5
3.00	0.3335	69.40	57.1
7.50	0.1334	27.76	71.8
15.00	0.0667	13.88	84.4
30.00	0.0333	6.94	99.8
75.00	0.0133	2.77	115.2
150.00	0.0066	1.39	130.0
300.00	0.0033	0.69	165.2
750.00	0.0013	0.27	190.5
1500.00	0.0006	0.14	209.2
3000.00	0.0003	0.07	225.7

Table XLII.—Conductivity of Cadmium Sulphate Calculated for Even Volumes.

$CdSO_4$.

v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.	v.	$\mu_{v_{25}°}$.
1	36.8	20	89.6	400	170.8
2	49.4	40	103.1	800	191.7
4	60.4	80	122.5	2000	214.7
8	72.6	200	150.7		

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of the double sulphate of ammonium and cadmium with the sum of the conductivities of its constituents, follows :

Table XLIII.—Comparison. Ammonium Cadmium Sulphate.

v.	$\mu_{v_{25}}$ $(NH_4)_2SO_4$.	$\mu_{v_{25}}$ $CdSO_4$.	Sum.	$\mu_{v_{25}}$ Double Salt.	Difference.
2	146.1	49.4	195.5	151.6	43.9
4	163.2	60.4	223.6	185.0	38.6
8	179.2	72.6	251.8	216.0	35.8
20	199.2	89.6	289.5	254.4	35.1
40	216.9	103.1	320.0	285.5	34.5
80	232.4	122.5	354.9	320.6	34.3
200	250.1	150.7	400.8	366.2	34.6
400	261.7	170.8	432.5	398.4	34.1
800	268.3	191.7	460.0	432.2	27.8
2000	276.6	214.7	491.3	474.0	27.0

Double Sulphate of Ammonium and Nickel.

The salt employed was analyzed and found to be pure. The solution used had the concentration 0.1337 normal, and a volume of 7.4795. This was diluted to volume 8, and this solution employed as the mother-solution for subsequent dilutions.

Table XLIV.—Conductivity of the Double Sulphate of Nickel and Ammonium.

Ammonium nickel sulphate, $(NH_4)_2SO_4.NiSO_4$. Molec. wt., cryst., 395.10.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}}$.
8	0.125	49.39	224.1
20	0.050	19.755	263.4
40	0.025	9.877	293.8
80	0.0125	4.938	322.3
200	0.0050	1.9755	370.1
400	0.0025	0.9877	404.6
800	0.00125	0.4938	439.4
2000	0.00050	0.19755	484.6

Nickel Sulphate.

The solution used had a concentration of 0.2295 normal, and a volume 4.3570. 272.31 cc. were diluted to 500 cc. to bring it

to a volume of 8, and this was used as the mother-solution for subsequent dilutions.

Table XLV.—Conductivity of Nickel Sulphate.

Nickel sulphate, $NiSO_4$. Molec. wt., 154.76.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$°.
8	0.125	19.34	77.9
20	0.050	7.738	96.1
40	0.025	3.869	109.0
80	0.0125	1.934	122.8
200	0.0050	0.7738	152.0
400	0.0025	0.3869	173.1
800	0.00125	0.1934	194.8
2000	0.00050	0.07738	232.3

The conductivity of ammonium sulphate has already been given.

Comparison of the conductivity of the double sulphate of nickel and ammonium, with the sum of the conductivities of its constituents, is given below:

Table XLVI.—Comparison. Ammonium Nickel Sulphate.

v.	$\mu_{v_{25}}$° $(NH_4)_2SO_4$.	$\mu_{v_{25}}$° $NiSO_4$.	Sum.	$\mu_{v_{25}}$° Double salt.	Difference.
8	179.2	77.9	257.1	224.1	33.0
20	199.9	96.1	296.0	263.4	32.6
40	216.9	109.0	325.9	293.8	32.1
80	232.4	122.8	355.2	322.5	32.9
200	250.1	152.0	402.1	370.1	32.0
400	261.7	173.1	434.8	404.6	30.2
800	268.3	194.8	463.1	439.4	23.7
2000	276.6	232.3	508.9	484.6	24.3

Double Sulphate of Potassium and Nickel.

The salt was made in the usual way by crystallization from a solution containing its constituents in equivalent proportions.

Analysis of crystallized $K_2SO_4.NiSO_4.6H_2O$:

	Calculated.	Found.
SO_4	43.93	43.82

The solution used was 0.1713 normal, and its volume 5.836. 364.75 cc. were then diluted to 500 cc. to bring it to volume 8, and this was employed as the mother-solution in subsequent dilutions.

Table XLVII.—Conductivity of Potassium Nickel Sulphate.

Potassium nickel sulphate, $K_2SO_4.NiSO_4$. Molec. wt., cryst., 435.24.

v.	Concentration.	Grams crystallized salt per liter.	$\mu_{v_{25}}$.
8	0.125	54.40	219.5
20	0.050	21.762	261.5
40	0.025	10.881	291.6
80	0.0125	5.440	323.7
200	0.0050	2.1762	369.4
400	0.0025	1.0881	400.2
800	0.00125	0.5440	438.0
2000	0.00050	0.21762	494.3

The conductivity of nickel sulphate has already been given.

The conductivity of potassium sulphate has been determined by a number of observers. We take the values of Jones and Mackay[1] obtained for 25°.

Table XLVIII.—Conductivity of Potassium Sulphate.

Potassium sulphate, K_2SO_4. Molec. wt., 174.36.

v.	Concentration.	Grams per liter.	$\mu_{v_{25}}$.
8	0.125	21.795	182.4
20	0.050	8.718	205.1
40	0.025	4.359	220.3
80	0.0125	2.1795	237.9
200	0.0050	0.8718	252.4
400	0.0025	0.4359	262.2
800	0.00125	0.21795	273.0
2000	0.00050	0.08718	276.5

Comparison of conductivity of double sulphate of potassium and nickel, with the sum of the conductivities of its constituents, is next given:

Table XLIX.—Comparison. Potassium Nickel Sulphate.

v.	$\mu_{v_{25}}$ K_2SO_4.	$\mu_{v_{25}}$ $NiSO_4$.	Sum.	$\mu_{v_{25}}$ Double salt.	Difference.
8	182.4	77.9	260.3	219.5	40.8
20	205.1	96.1	301.2	261.5	39.7
40	220.3	109.0	329.3	291.6	37.7
80	237.9	122.8	360.7	323.7	37.0
200	252.4	152.0	404.4	369.4	35.0
400	262.2	173.1	435.3	400.2	35.1
800	273.0	194.8	467.8	438.0	29.0
2000	276.5	232.3	508.8	494.3	14.5

[1] Diss., Johns Hopkins University, 1896; This JOURNAL, 19, 83.

The results with double sulphates show that all of them remain undissociated to about the same extent. In a half-normal solution the "difference" amounts, in the case of ammonium magnesium snlphate, to 25 per cent; in ammonium copper sulphate to 29 per cent; in ammonium ferrous sulphate to 23 per cent; in ammonium cadmium sulphate to 22 per cent of the sum of the individual conductivities of the constituents. In the cases of nickel ammonium and nickel potassium sulphates the difference at a volume 8 about equals that of the other sulphates at the same dilution; more concentrated solutions were not measured, since these salts are not sufficiently soluble.

Klein[1] showed that a mixture of sodium and potassium sulphates has a conductivity which is about 1 per cent less than that calculated from its constituents. The difference here is much larger. Jones and Mackay[2] found a greater difference in the alums studied by them—from 2.5 to 11 per cent.

This would seem to indicate that the double sulphates which are not alums exist to a greater degree undissociated in aqueous solution than the alums. The difference was found to disappear at a dilution of about 400 liters in the case of the alums, while in the case of the sulphates under investigation it did not disappear at a dilution of 2000.

DIRECT COMPARISON OF DOUBLE SALT AND MIXTURE.

Through the work referred to in this paper the conclusion has been reached that double salts in concentrated solution dissociate to a greater or less extent as if they were salts of complex acids, and then, as the dilution increases, the complex ion dissociates into simpler ions.

The question now arises, is the state of equilibrium the same in a solution of a double salt as it is in a mixture of solutions of the constituents having the same concentration as the double salt? It seemed desirable to test this question as thoroughly and carefully as possible. Mr. C. F. Lindsay[3] has already obtained some very interesting results bearing on this problem. He found that the conductivities of mixtures of the

[1] Wied. Ann., 27, 151.
[2] *Loc. cit.*
[3] This JOURNAL, 25, 62.

constituents were always slightly larger than those of the double salt at the same dilution. On account of the very unexpected and surprising results obtained, we have repeated some of his work, and also studied the question with other substances.

The method of work was the same as that described above. The solution of the double salt was carefully standardized and the conductivity determined. Then a solution of each of the constituent salts was prepared and accurately standardized. From these analyses the volumes of the two solutions, which would contain the salts in the same proportion in which they exist in the double salt, were calculated. These volumes of the two solutions were mixed in a measuring flask, and the whole diluted to a known volume. This mixture was then standardized gravimetrically to see that no error had been made in bringing the constituents together and in the dilution. This standardized solution, which in every case was found to contain the constituents to almost exactly the extent calculated, was used as the mother-solution in subsequent dilutions.

The same cell was used to measure the conductivity of the double salt as was employed with the mixture, and they were generally measured as nearly as possible at the same time, in order that the temperature of the thermostat (which was regulated within 0°.1 by an Ostwald regulator) might be the same. The same apparatus was used throughout with the double salt and the mixture.

Lindsay obtained the following results:

Table L.—Double Chloride of Potassium and Cadmium.

$KCl.CdCl_2$.

v.	Double salt, $KCl.CdCl_2$.	Mixture, $KCl + CdCl_2$.	Difference.
	μ_v.	μ_v.	
2	117.8	119.4	1.6
4	146.3	148.1	1.8
8	172.4	174.9	2.5
20	208.4	209.3	0.9

The conductivity of the double chloride is, thus, less than the conductivity of the mixture of the two chlorides. The

difference in this case and in all other cases tried, is always small, but is larger than all known experimental errors, and is always in the same direction; *i. e.*, the mixture has the higher conductivity.

Table LI.

Double sulphate of potassium and nickel, $K_2SO_4.NiSO_4$.

v.	Double salt. $K_2SO_4.NiSO_4$.	Mixture. $K_2SO_4.NiSO_4$.	Difference.
	μ_v.	μ_v.	
6	213.68	216.31	2.63
12	244.38	246.61	2.23
24	273.31	276.02	2.71
60	314.13	314.35	0.22

Table LII.

Double sulphate of ammonium and magnesium, $(NH_4)_2SO_4.MgSO_4$.

v.	Double salt. $(NH_4)_2SO_4.MgSO_4$.	Mixture. $(NH_4)_2SO_4 + MgSO_4$.	Difference.
	μ_v.	μ_v.	
2	159.7	164.6	4.9
4	197.7	202.4	4.7
8	231.5	237.1	5.5
20	273.9	277.9	4.0

We repeated the work of Lindsay with ammonium magnesium sulphate, and also studied in this connection ammonium cadmium sulphate. We obtained the following results:

Table LIII.

Ammonium magnesium sulphate, $(NH_4)_2SO_4.MgSO_4$.

v.	Double salt. $(NH_4)_2SO_4.MgSO_4$.	Mixture. $(NH_4)_2SO_4 + MgSO_4$.	Difference.
	μ_v.	μ_v.	
5.09	212.70	216.78	4.08
10.18	243.89	248.28	4.39
25.46	284.80	289.10	4.30
Repeated, making and standardizing solutions anew.			
3.09	189.9	193.2	3.3
Repeated, making and standardizing solutions anew.			
6.064	216.03	219.96	3.93

Table LIV.

Ammonium cadmium sulphate, $(NH_4)_2SO_4.CdSO_4$.

v.	Double salt, $(NH_4)_2SO_4.CdSO_4$.	Mixture, $(NH_4)_2SO_4 + CdSO_4$.	Difference.
	μ_v.	μ_v.	
3.036	171.94	173.25	1.31
3.001	171.7	172.4	0.7

From these results the conclusion is reached that the conductivity of a double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt. It thus appears fairly certain from the work of Lindsay and from our own, that the double salt, when once formed, does not dissociate in exactly the same way or to the same extent as the mixture of the constituents which have never united to form the double salt.

CRYOSCOPIC MEASUREMENTS.

The application of the freezing-point method to the problem of the condition of double salts in solution has already been made by several. Jones and Mackay[1] found from the study of the alums results which led to the same general conclusions as those obtained by the conductivity method. Jones and Ota attempted to apply the freezing-point method to solutions of double chlorides, but obtained results of an entirely unexpected character. The molecular conductivities beyond a certain concentration increased with the concentration to a very marked extent. Phenomena similar to these have since been studied by Jones and Chambers,[2] and later by Chambers and Frazer.[3]

We have applied the freezing-point method to a number of the substances whose conductivities we have studied in order to see whether normal values would be obtained, or whether they would give such apparently abnormal results as had been obtained by Jones and Chambers, and by Chambers and Frazer. The following results were obtained with the double cyanide of potassium and mercury :

[1] *Loc. cit.*
[2] This JOURNAL, **23**, 89.
[3] *Ibid.*, **33**, 512.

Table LV.—Double Cyanide of Potassium and Mercury, $K_2Hg(CN)_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.442	156.74	0.4095	1°.902	4.64
4.884	78.37	0.2047	0°.971	4.74
12.210	27.35	0.0819	0°.405	4.94

Table LVI.—Mercuric Cyanide, $Hg(CN)_2$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
5	50.476	0.2	0°.387	1.93

Table LVII.—Potassium Cyanide, KCN.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
1.1034	59.08	0.9063	3°.385	3.73
1.4343	45.45	0.6972	2°.623	3.76
2.8686	22.72	0.3486	1°.321	3.79
7.4129	8.79	0.1349	0°.531	3.93

Table LVIII.—Comparison. Potassium Mercuric Cyanide.

v.	2Δ KCN.	*v.*	Δ $Hg(CN)_2$.	Sum.	Δ Double salt.	Difference.
2.5	7.57	5	1.93	9.50	4.73	4.77

In the above and following results v is the volume of the solution, L the lowering of the freezing-point actually observed, and Δ the molecular lowering of the freezing-point.

The freezing-point lowerings of this double salt and its constituents are normal; *i. e.*, the molecular lowerings increase from the most concentrated to the most dilute solutions.

Table LIX.—Potassium Cadmium Iodide, K_2CdI_4.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.302	303.08	0.4344	3°.878	8.927
2.762	252.56	0.362	3°.177	8.776
5.524	126.28	0.181	1°.557	8.602
9.207	75.77	0.1086	0°.960	8.84
13.810	50.51	0.0724	0°.664	9.17

This salt shows a minimum in the curve of molecular depressions between the volumes 2.7 and 5.5 or between the volumes 5.5 and 9.2. The comparison with its constituents was therefore not attempted, and the molecular depressions produced by the constituents were not ascertained.

These results are strikingly analogous to those already found. The molecular lowering decreases with the dilution up to a certain point, reaches a minimum, and then increases from this point with further increase in dilution. The concentration at which this minimum was observed in the molecular lowering was found to vary somewhat with the nature of the substance, but it usually occurred at a dilution of from 0.1 to 0.2 normal. It occurs at this same concentration in the double iodide, as can be seen from Table LIX.

RESULTS WITH SULPHATES.

Table LX.—Ammonium Cadmium Sulphate, $(NH_4)_2SO_4.CdSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
1.6347	202.03	0.6117	3°.052	4.99
2.0433	161.64	0.4894	2°.493	5.09
2.7248	121.11	0.3670	1°.914	5.21
4.0866	80.82	0.2447	1°.345	5.49
8.1732	40.41	0.1223	0°.719	5.88
16.3464	20.20	0.0612	0°.378	6.17

Table LXI.—Cadmium Sulphate, $CdSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
0.7502	277.30	1.3328	2°.526	1.89
1.0004	207.97	0.9996	1°.774	1.77
1.5004	138.64	0.6664	1°.175	1.73
1.876	110.89	0.533	0°.933	1.75
2.500	83.22	0.400	0°.714	1.78
3.752	55.13	0.2665	0°.505	1.89
7.504	27.56	0.1333	0°.263	1.93

Table LXII.—Ammonium Sulphate, $(NH_4)_2SO_4$.[1]

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
5.0	26.432	0.2	0°.829	4.14
10.0	13.216	0.1	0°.437	4.37
14.28	9.2512	0.07	0°.316	4.51
20.00	6.608	0.05	0°.237	4.74
33.33	3.9648	0.03	0°.148	4.93
66.66	1.9824	0.015	0°.075	5.00

Table LXIII.—Comparison. Ammonium Cadmium Sulphate.

v.	Δ $CdSO_4$.	Δ $(NH_4)_2SO_4$.	Sum.	Δ Double salt.	Difference.
5	1.90	4.14	6.04	5.57	0.47

Table LXIV.—Ammonium Copper Sulphate, $(NH_4)_2SO_4.CuSO_4$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
3.069	130.32	0.3258	1°.736	5.32
6.138	65.16	0.1629	0°.990	6.07

Of the sulphates studied, only cadmium sulphate shows a minimum in the molecular lowering of the freezing-point.

DOUBLE NITRATE OF PRASEODYMIUM AND AMMONIUM.

Table LXV.—Praseodymium Nitrate, $Pr(NO_3)_3$.

v.	Grams per liter.	Concentration.	Lowering. L.	Molecular depression. Δ.
2.6305	124.15	0.38015	2°.184	5.74
5.2610	62.07	0.19007	1°.054	5.53
10.5220	31.03	0.09503	0°.543	5.71
21.0440	15.51	0.04752	0°.284	5.97

This salt does not give a regular rise in the molecular depression with increasing dilution, but decreases, reaching a minimum between the volumes 2 and 10. It therefore falls in the same category with those salts described by Jones and Chambers.[2]

[1] Jones and Mackay: *Loc. cit.*

[2] This JOURNAL, **23**, 89.

Table LXVI.—Molecular Lowering of Praseodymium Nitrate Calculated for Even Volumes.

v.	Concentration.	Molecular lowering. Δ.
2	0.5	5.79
4	0.25	5.63
8	0.125	5.63
20	0.050	5.95

Table LXVII.—Ammonium Nitrate, NH_4NO_3.

v.	Concentration.	Grams per liter.	Lowering. L.	Molecular depression. Δ.	Twice the molecular depression. 2Δ.
1	1.0	80.12	3°.136	3.13	6.27
2	0.5	40.06	1°.629	3.26	6.52
4	0.25	20.03	0°.863	3.45	6.90
10	0.10	8.012	0°.363	3.63	7.26

Table LXVIII.—Ammonium Praseodymium Nitrate, $2NH_4NO_3.Pr(NO_3)_3$.

v.	Concentration.	Grams per liter.	Lowering L.	Molecular depression. Δ.
0.8314	1.2027	568.40	16°.5	13.71
1.6628	0.6013	284.20	7°.5	12.47
3.3256	0.3006	142.10	3°.637	12.09
8.314	0.12027	56.84	1°.779	14.79
16.628	0.06013	28.42	0°.887	14.79

This double salt exhibits the minimum in the molecular depression. As this is not observed in the case of ammonium nitrate, and is observed in praseodymium nitrate, we must ascribe it to the influence of the praseodymium nitrate.

Table LXIX.—Molecular Depression of Ammonium Praseodymium Nitrate Calculated for Even Volumes.

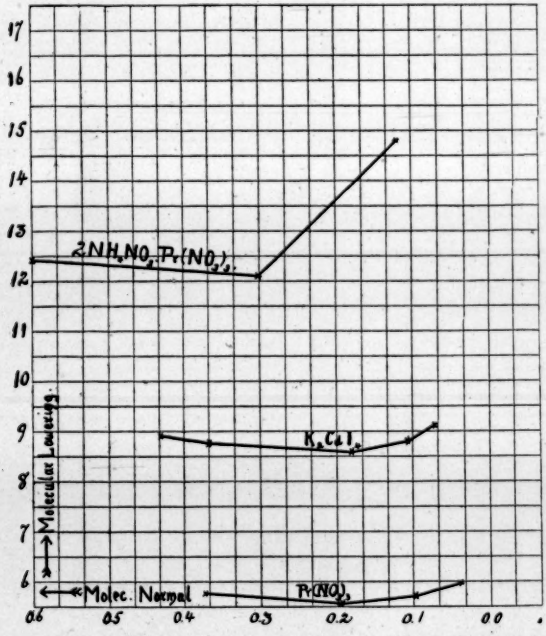
v.	Concentration.	Molecular depression. Δ.
2	0.5	12.40
4	0.25	12.45
8	0.125	14.63
20	0.050	

Table LXX.—Comparison. Ammonium Praseodymium Nitrate.

v.	2Δ NH_4NO_3.	*v.*	Δ $PrNO_3$.	Sum.	Δ Double salt.	Difference.
1	6.27	2	5.79	12.06	12.40	—0.36
2	6.52	4	5.63	12.15	12.45	—0.30
4	6.90	8	5.63	12.53	14.63	—2.10
10	7.26	20	5.95	13.21		

A minimum in the molecular lowering exists in praseodymium nitrate at a concentration of about 0.2 normal. A minimum occurs in the molecular lowering of the double nitrate at about the same concentration, as has been pointed out.

In order that these minima in the molecular lowering may be seen more clearly, some of our results are plotted in curves. The ordinates are molecular lowerings and the abscissas are concentrations.



Jones and Chambers[1] have offered a possible explanation of these minima in the freezing-point curves. Since the molecular

[1] This JOURNAL, **23**, 103.

lowerings in the very concentrated solutions are much larger than would be expected, they suggest that in these concentrated solutions the dissolved substance has combined with a portion of the solvent, forming compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The total amount of the solvent present is diminished by just so much as has combined with the dissolved substance. The freezing-point lowering is abnormally great because a part of the water is no longer present as solvent, but is in combination. They refer to a number of cases where definite compounds between water and the dissolved substance are known to exist in concentrated solutions.

It is impossible to say at present whether or not this explanation is the true one. We accept it tentatively, as we are not prepared to offer any other theory to account for the facts.

SUMMARY.

We are led from the results of the study of the electrical conductivity of the solutions investigated, to the conclusion that the double iodides of strontium and cadmium and of potassium and cadmium exist in concentrated solution to a considerable extent undecomposed. They do not break down very readily, but retain their compound nature even at moderately high dilutions. The same thing is found to be true of the double nitrates of ammonium with praseodymium and neodymium, and of the double cyanide of potassium and mercury. The nitrates, however, break down at comparatively low dilutions. The double sulphates of ammonium with cadmium, copper, magnesium, iron, nickel, as well as that of potassium and nickel, appear not only to remain undissociated to some extent in concentrated, but even in dilute solutions they are not completely dissociated into their constituents.

A study of the conductivities of certain mixtures and double salts showed that the state of equilibrium is not necessarily always the same in the two cases at the same concentration. While the double salt may not be completely dissociated into its constituents at any given dilution, the constituents do not combine to form the same amount of double salt when brought together at that dilution.

Cadmium sulphate, potassium cadmium iodide, praseodymium nitrate, and ammonium praseodymium nitrate, are substances whose molecular lowering of the freezing-point of water does not increase regularly with the dilution, but there exists a well-defined minimum in the molecular lowering, and this occurs for each of the above substances at a dilution not widely removed from 0.2 normal. As the concentration increases from this point the molecular lowering may increase very considerably.

We had hoped to electrolyze solutions of the double salts employed in this work, to determine if possible the nature of the complex anions. We propose to carry out such an investigation in the future.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1901.

Contribution from the Labratory of General Chemistry, University of Michigan.

ON THE CONSTITUENTS OF JAMAICA DOGWOOD.

BY PAUL C. FREER AND A. M. CLOVER.[1]

The Jamaica dogwood (*Piscidia Erythrina, Linné*) is a tree, usually about 20 feet in height, belonging to the order of Leguminosae, having its habitat in the West Indian Islands and adjacent mainland. The portion used is the bark of the root, and the active principle was supposed to be a resinoid called piscidine, which was said to crystallize from alcohol in colorless prisms, melting at 192°. As will be shown below, this principle, in reality, is not a chemical individual, but it consists of two very distinct bodies.

The material used in the investigation was the pulverized bark of the root and, of the series of extracts, that with water contained the greatest quantity of solid matter, this solution, the chief portion of the residue of which is the calcium salt of a new acid, will therefore be considered first.

Aqueous Solution—Piscidic Acid.

The pulverized bark was placed in 10-gallon crocks, about

[1] Parke, Davis & Co. Fellow in the University of Michigan. This work was undertaken with materials furnished by Messrs. Parke, Davis & Co. and at their suggestion, in order to clear up the chemistry of a most interesting plant, from a purely scientific standpoint. Our thanks are due to Messrs. Parke, Davis & Co. for their willing assistance and unflagging interest.

10 pounds to each vessel. It was then covered with pure water and allowed to stand for three or four days, being thoroughly stirred from time to time, and finally the liquid was siphoned off, this operation being repeated until no further substance went into solution. The united, straw-colored extract was then gently evaporated on a water-bath until it had diminished to one-fourth of its original bulk. Samples of this concentrated extract, when evaporated to dryness, demonstrated the presence of a very deliquescent calcium salt of an organic acid. This calcium salt can be separated from the concentrated aqueous solution by the addition of alcohol, in which it is insoluble, and filtering the precipitate. After heating with water containing animal charcoal, it can, on evaporation, be separated in colorless crystals, from which the pure acid can be obtained by solution in water, precipitation with lead acetate, decomposition of the white lead salt with hydrogen sulphide in alcoholic suspension, and evaporation of the solution. However, this method is rather tedious, and it also involves the use of considerable alcohol, so that it is better, although it does not at first yield so pure an acid, to proceed as follows: The concentrated aqueous solution is first precipitated with a solution of lead acetate in sufficient quantity to separate all of the coloring-matter along with the lead salt of a portion of the acid. This brownish precipitate is filtered and the clear filtrate once more precipitated with lead acetate, care being taken not to separate all of the acid in this way, as the very last portions of the lead salt are impure. The nearly pure lead salt is washed repeatedly by decanting with water. It is finally poured on a large suction-filter and dried as well as possible. As it filters with great difficulty, it is advisable to have as little liquid as possible during this last stage. The lead salt is finally suspended in a sufficient quantity of alcohol to make a thin paste and completely decomposed with hydrogen sulphide. The alcoholic solution, after filtering, is first concentrated by distilling off the alcohol *in vacuo*, until the bulk has decreased to about one-sixth. It is then placed in large dishes and evaporated in the cold. There remains a thick syrup, which is sometimes permeated with a few crystals (ethyl ether of the acid), the whole finally solidifying to

a mass of radiating needles. The acid is extremely soluble in water, slightly so in ether; insoluble in chloroform, benzene, and ligroin.

In order to purify the substance it is placed in a Soxhlet extractor and exhausted with ether, when an insoluble residue, consisting mainly of calcium salt, remains. The ethereal solution, on evaporation, is free from inorganic residue, and deposits the acid in sticky lumps somewhat resembling glucose. This remainder is then dissolved in a little alcohol, about twice the volume of ether added, and chloroform poured in until precipitation begins. On scratching the sides of the flask with a glass rod, feathery concentric crystals are deposited, the melting-point of which is 182° to 185°, decomposition, with evolutions of carbon dioxide, beginning at 185°. For analytical purposes, the acid was recrystallized from methylpropylketone, which seems to be the only solvent from which it is at once deposited in crystals on cooling. The crystals obtained from the latter solvent, however, retain methylpropylketone very obstinately, so that the last traces can be expelled only by continued heating at 110° to 120°.

The samples analyzed were recrystallized three times from methylpropylketone and dried at 110°.

I. 0.2091 gram substance gave 0.3941 gram CO_2; and 0.0910 gram H_2O.

II. 0.1880 gram substance gave 0.3524 gram CO_2; and 0.0836 gram H_2O.

	Calculated for $C_{11}H_{18}O_7$.	Found. I.	Found. II.
C	51.5	51.45	51.11
H	4.7	4.84	4.93

No account of an acid of this composition, with the properties of ours, has been found in the literature, so that we have given to the one above described the name piscidic acid.

The properties of piscidic acid are very much like those of mucic or saccharic acid. It decomposes on heating, giving an odor of caramel, and finally chars, leaving a porous coke. It is instantly oxidized by potassium permanganate, forming potassium carbonate, oxalate, and apparently formate, so that complete destruction of the molecule takes place.

Piscidic acid is dibasic, as is shown by the following experiment:

N/8 NaOH solution was just neutralized with pure recrystallized acid, the conductivity (equivalent) determined at N/32 and N/1024.

	Bridge.	Resistance out.	T. 25°, equiv. acid.
λ_{32}	426.4	100	
	450.6	110	λ 68.9
	493.0	130	
λ_{1024}	474.6	3000	λ 88.8
	499.2	3300	
	507.0	3400	λ 89.2

$$\frac{\lambda_{1024}-\lambda_{32}}{10} = 2.0+.$$

According to Ostwald's law[1] the acid is consequently dibasic. The acid value gave the following results:

1. 0.3503 gram substance took 27.4 cc. N/10 KOH to neutralize it.

Equivalent weight = 128; molecular weight = 256.

2. Determined from different sample: 0.3390 gram substance took 25.9 cc. N/10 KOH.

Equivalent weight = 130.8; molecular weight = 251.6; Calculated molecular weight, 256.

It is evident that a combination of basicity determinations by means of the electric conductivity, and of the acid value of any acid must give the molecular weight.

Piscidic acid is therefore a dibasic acid and evidently contains two carboxyl groups, as the following experiment shows:

0.5 gram of the acid were mixed with 0.5 gram resorcin and then heated in an oil-bath to 180° for fifteen minutes. 0.2 gram freshly fused zinc chloride was then added to the mass, and the temperature gradually increased to 210°, where it was kept for half an hour. When cold, the product was taken out, washed with hydrochloric acid, and finally a trace dissolved in caustic soda and diluted with water. The result was an intense fluorescence. The two carboxyl groups evidently must be in the γ, γ' positions as in phthalic or succinic acids. The resulting formula of the acid is, therefore,

$$C_9H_{10}O_3(CO_2H)_2.$$

[1] Ostwald: Ztschr. phys. Chem., 1, 74; 2, 901.

Ethyl Ester—Three grams of piscidic acid were dissolved in absolute alcohol, 10 drops of hydrochloric acid added, and the whole boiled on the water-bath for two or three hours, the alcohol was then gently evaporated and the whole allowed to crystallize. The ester was recrystallized from hot water. It separated in shiny needles, melting at 207°–208°, softening at 204°. This substance is the acid ester, as is shown by the fact that it dissolves in sodium carbonate, and this is a further proof of the relative positions of the two carboxyl groups. The same ester is formed in limited quantities during the original isolation of the acid, provided hydrochloric acid is present during the extraction, the alcohol necessary being present during the precipitation of the lead salt with hydrogen sulphide.

I. 0.2240 gram substance gave 0.4579 gram CO_2; and 0.1134 gram H_2O.

II. 0.1976 gram substance gave 0.4010 gram CO_2; and 0.988 gram H_2O.

	Calculated for $C_{18}H_{16}O_7$.	Found. I.	II.
C	54.9	55.02	55.34
H	5.6	5.62	5.56

The acid value of the ester confirms this analysis:

0.6139 gram substance took 43.4 cc. of N/10 potassium hydroxide to neutralize it after heating on a water-bath for one-half hour.

Calculated molecular weight, 284; found molecular weight, 283.

The substance, after saponification as above, was treated with the equivalent quantity of sulphuric acid, evaporated to dryness, and the residue extracted with a little alcohol, ether, and chloroform, and stood aside to crystallize. The result was the production of the original acid.

The acid ester was boiled with absolute alcohol and sulphuric acid for several hours, but no further change took place; the neutral ester cannot be produced in this way.

Aniline Salt and Anilide.—Two grams of acid in 10 cc. of alcohol were treated with 1.5 grams of aniline, and gently warmed for a few minutes. On standing, shiny, white plates of the aniline salt crystallize (melting-point 149°). This salt,

heated for two hours at 170° to 180°, gives off water and leaves a thick syrup, which cools to a resinous mass. On being covered with alcohol, it dissolves gradually and a white solid is precipitated on standing. Recrystallized from alcohol and water, and finally from ether, it separates in white needles, melting at 196°.

I. 0.1439 gram substance gave 0.3600 gram CO_2; and 0.0729 gram H_2O.

II. 0.1476 gram substance gave 0.3693 gram CO_2; and 0.764 gram H_2O.

III. 0.197 gram substance gave 13 cc. N at 23° and 733 mm.

	Calculated for $C_{28}H_{28}N_2O_5$.	Found. I.	II.	III.
C	67.98	68.23	68.24	....
H	5.42	5.63	5.42	....
N	6.89	....	....	7.09

This substance is therefore the dianilide. A molecular weight determination, by the boiling-point method in ethyl alcohol gave results showing a gradual rise in molecular weight with increased amount of substance, results in accord with Auwers' experience with anilides and hydroxy-compounds.[1]

Solvent.	Substance.	Δ.	M.	Calc. M.
17.496	0.558	0.097	378.2	406
	1.151	0.189	400.7	
	1.798	0.285	415.0	
	2.347	0.366	421.7	

A neutral solution of piscidic acid is not precipitated by copper or barium salts; mercuric salts precipitate slightly yellow, silver nitrate white, the silver salt rapidly turning black. The lead salt is white and stable.

In order to learn more in regard to the constitution of the acid, it was heated with hydriodic acid, in order to determine methoxy groups according to Zeisel's method, but with entirely negative results, no methoxy groups being present. The acid was finally heated in a sealed tube to 100° with hydriodic acid (sp. gr. 1.96) without producing methyl iodide. The reaction-product consisted for the greater part of oily and tarry substances from which only a small quantity of a solid

[1] Ztschr. phys. Chem., 23, 449; 30, 529.

substance, in yellow needles, melting at 120°, could be isolated, the quantity being too little for analysis. Hydrobromic acid (sp. gr. 1.12) even at 150° for several hours, seems to have no effect, the unchanged acid being recovered. It is therefore safe to assume that no saponifiable groups are present.

In order to ascertain the number of hydroxyl groups present, attempts were made to obtain an acetyl derivative of the acid; however, the resulting substance was an oil which could not be crystallized. Better results were obtained with the ethyl ester.

Three and a half grams ethyl ester were covered with 20 grams of pure acetic anhydride, sealed in a tube, and heated for five hours at 100°. After cooling, the tube contained a clear, slightly yellow liquid. This was added to water and the water gradually neutralized in the cold with sodium carbonate, finally in excess. There remained a small quantity (0.75 gram) of an insoluble thick resin, the remainder dissolved. The colorless solution was filtered through wet filter paper and exhausted with ether. It was then acidified and again extracted with ether, dried over calcium chloride, evaporated to three-quarters, and then placed in a crystallizing dish in a vacuum. There remained a colorless resin which, on being covered with dry ether and rubbed with a glass rod, finally crystallized in white, rhombic flakes, melting at 149° to 151°.

0.1449 gram substance gave 0.2953 gram CO_2; and 0.0717 gram H_2O.

	Calculated for $C_{17}H_{30}O_9$.	Found.
C	55.4	55.6
H	5.4	5.4

I. 0.5272 gram substance took 14.0 cc. N/10 KOH to neutralize it.

II. 0.5430 gram substance took 14.3 cc. N/10 KOH to neutralize it.

Calculated molecular weight 368; found 376 and 379.

For saponification, an excess of a N/10 potassium hydroxide was added, and the whole warmed. On completion of the re-

action it was found, however, that the caustic potash used was far in excess even of that called for by five acetyl groups, an obvious impossibility, so that the conclusion was reached that potash in excess decomposes the acid completely. A determination of acetyl groups with baryta gave results which agreed approximately with two acetyl groups, but these were too low. There cannot be much doubt that this is a diacetyl derivative.

Fusion of the acid with potash resulted in complete decomposition, no satisfactory results being obtained. The acid evidently does not contain an aromatic group, its extreme solubility in water, its resemblance to saccharic acid, the impossibility, so far, of isolating an aromatic derivative from it, all speak in favor of its being a member of the aliphatic series.

Bromine, in absolute chloroform solution, attacks the acid slowly; apparently no addition-product is produced, as hydrobromic acid is given off from the start. In aqueous solution, bromine reacts steadily. Two grams of the acid were dissolved in as little water as possible, and then bromine water added gradually until a permanent color appeared. The solution was then evaporated at ordinary temperatures, under which conditions colorless prisms separated, which, recrystallized from water, yield silky, concentric needles, melting at 234° to 236°, with decomposition and separation of hydrobromic acid. The analyses agree best with the figures calculated for a dibromine addition-product, and not for a body produced by substitution.

	Calculated for $C_{11}H_{10}O_7Br_2$.	Calculated for $C_{11}H_{12}O_7Br_2$.	Found.
C	31.8	31.7	30.91
H	2.39	2.85	2.75
Br	38.6	38.4	37.58

The quantity of acid at our disposal was not sufficient to enable us to carry on experiments which would settle the constitution of piscidic acid definitely, but we hope at some future time again to take up the subject of this interesting acid and definitely settle its structure. Its structure, as far as is yet known, is represented by $C_9H_8O(OH)_3(CO_2H)_2$.

EXTRACTS FROM THE BARK OF JAMAICA DOGWOOD WITH SOLVENTS OTHER THAN WATER.

Chloroform Extract.

Chloroform extracts all of the crystalline constituents of the Jamaica dogwood bark, excepting piscidic acid and one other body, which occurs in the solution formed with ligroin. Amorphous substances, mainly consisting of cutose, are not taken up by the solvent, and, as a consequence, the individual substances can be isolated in a pure state. The methods of isolation of the various products will be described first, the properties and reactions subsequently.

Fifteen pounds of ground bark were thoroughly exhausted with chloroform; 90 grams of residue, which solidified on cooling, remaining after evaporating the solvent on a water-bath. This residue was dissolved in 400 cc. of chloroform and allowed to stand for several days. A white precipitate (8 grams) deposited in the bottom of the flask. This was filtered, washed well with chloroform, and dried. It contained a body which, when pure, melts at 150° to 155°.

The chloroform filtrate was evaporated to half of its original volume, diluted with an equal volume of ether, and then extracted with caustic potash (100 grams to 300 cc. of water), the whole being carefully cooled. The caustic potash solution turns deep-red, and takes up over one-half of the contents of the chloroform-ether. The latter was repeatedly washed with water until this solvent became colorless, then with a trace of acid, finally dried over calcium chloride, and ether-chloroform distilled. The residue obtained in this way will be described first, the alkaline extract second.

A. Neutral Residue from Ether-Chloroform Extract.—After distilling off the chloroform the residue, after extraction with caustic potash, was covered with 200 cc. of ether. Crystallization soon begins and continues for several hours. The residue is then filtered and well washed with ether. The crystals (10 grams), after being dried on a porous plate, were purified further by boiling out with about a liter of ligroin, a white amorphous substance being removed thereby. The remainder now consisted of two bodies which could be separa-

ted by fractional crystallization as follows: A hot alcoholic solution of the two is allowed to cool without stirring; one of the bodies, melting at 216°, then separates before the other, and can be filtered, the other finally coming down on longer standing (melting-point 201°).

The body melting at 216° consists of yellow, light, and very fine needles; that melting at 201° consists of colorless, heavy prisms. The proportions are one to five.

Ether Solution Filtered from the Substances that Melt at 201° and 216°.—After distilling the solvent, the residue weighed 25 grams. It was dissolved in 100 cc. of ether and allowed to stand over calcium chloride. When dry, it was treated with about five volumes of ligroin, the flask being well shaken during the addition. A precipitate is formed which settles to the bottom in a slightly caked condition, so that the supernatant liquid can be decanted; afterward, the precipitate is rendered perfectly granular by shaking with a small quantity of ligroin.[1] Quantity, 10 grams.

The solvent, after filtration, was concentrated and completely freed from volatile matter. It was then washed with 70 per cent alcohol (which removed some of the substance melting at 50° to 80° mentioned in the foot-note), and finally heated in a pressure-flask with alcoholic potash at 100° for several hours. The alcoholic solution, when evaporated and extracted with ether, yielded a considerable quantity of non-saponifiable matter[2] which crystallized from alcohol in colorless flakes, melting at 123° to 125°, probably some complex alcohol formed during saponification. The ethereal mother-liquors deposited a further quantity of substance on fractional crystallization, together with a considerable quantity of amorphous matter, which, separating in the first section, was discarded.

B. Alkaline Solution from Ether-Chloroform Extract.—More than half the original chloroform-ether extract was removed by caustic potash, the solution having a deep red color. It

[1] The solvent from the above, on concentration, deposits a small quantity of crystals (melting at 80°, softening at 50°). These were proved to be identical with the preceding substance.

[2] The ether extract of the acidified solution gave a small quantity of the fatty acid.

was neutralized, the precipitate filtered, washed, and dried. It is quite soluble in sodium carbonate and in alcohol, and it is completely taken up by a sufficient quantity of ether. The substance is amorphous and is a resin. All attempts to isolate a crystalline body were fruitless.

That the substances described above are not decomposition-products, produced by the action of the alkali during extraction, is shown by the fact that all were identified in the ligroin solution.

Ligroin Extract.—The ground bark was thoroughly exhausted with low-boiling ligroin (distilling on a water-bath), the solvent evaporated on a water-bath, and finally completely removed under diminished pressure. The residue was then dissolved in ether and the resulting solution allowed to evaporate slowly in the air. Crystals of the yellow body, melting at 216°, formed throughout the liquid, while at the bottom, a light-colored deposit formed. After a time the mother-liquor was decanted and the sediment washed with several small portions of ether, by which means it was possible to remove nearly all of the yellow substance. The residue, when pure, consists of a body which melts at 159°, and a small portion of the solid previously described as melting at 201°. On further standing, the ethereal solution deposited further quantities of the mixture, the amount of the substance melting at 201° steadily increasing. The two substances were separated by means of benzene, the substance melting at 201° being only sparingly taken up by this solvent, while that fusing at 159° dissolves quite readily.

The ethereal solution, after decantation, yields the substance mentioned above, melting at 50° to 80°, as a precipitate, when it is mixed with ligroin.

The ligroin extract therefore yields all of the neutral substances found in the chloroform with one addition. The detailed description of the various substances which were isolated follows:

Substance $C_{28}H_{30}O_7$; Melting-point 201°.

The crude substance was purified by recrystallizing it from alcohol. By allowing it to separate slowly, it is obtained in

highly refractive rectangular prisms, some of which have wedge-shaped ends. It is very soluble in chloroform, moderately so in benzene and acetic acid, sparingly in alcohol, and practically insoluble in ether and ligroin. It is insoluble in alkali.

I. 0.2428 gram substance gave 0.6015 gram CO_2; and 0.1092 gram H_2O.

II. 0.2734 gram substance gave 0.6779 gram CO_2; and 0.1278 gram H_2O.

	Calculated for $C_{23}H_{20}O_7$.	Found. I.	II.
C	67.65	67.56	67.62
H	4.90	4.99	5.19

A molecular weight determination in naphthalene gave:

Solvent. Grams.	Substance. Gram.	Δ.	M.	Calculated molecular weight.
18.838	0.1923	0.175	409	408
"	0.4679	0.440	399	

From these and later considerations, the formula is shown to be $C_{23}H_{20}O_7$. The substance is decomposed by methyl alcoholic potash, two different crystalline products being obtained under different conditions.

1. Five grams of the body were boiled in a flask connected with a reflux condenser with 10 grams caustic potash in 500 cc. methyl alcohol for ten to twelve hours. The solution was then neutralized with hydrochloric acid, the alcohol nearly distilled off, the whole then acidified and precipitated with water, the precipitate filtered, washed, dried, and dissolved in a mixture of chloroform and ether, the latter then being extracted with a solution of caustic potash. This, when acidified, yielded a precipitate which, after being washed and dried, was recrystallized from alcohol, when it melted at 159°. The crystals consist of square, yellow plates, which are soluble in alcohol and chloroform, sparingly so in ether and benzene. The substance dissolves in a warm solution of sodium carbonate, but is precipitated on cooling. The yield was only about 35 per cent, the rest being recovered in unchanged condition. An analysis of a pure sample dried at 105° gave:

I. 0.1855 gram substance gave 0.4356 gram CO_2; and 0.0785 gram H_2O.

II. 0.2487 gram substance gave 0.5852 gram CO_2; and 0.1040 gram H_2O.

III. 0.1558 gram substance gave 0.3659 gram CO_2; and 0.0700 gram H_2O.

	Calculated.	Found. I.	II.	III.
C	64.08	64.04	64.17	64.05
H	4.85	4.85	4.65	4.99

A molecular weight determination, which will be given below, makes the formula $C_{22}H_{20}O_8$ appear probable.

The substance takes up bromine readily.

2. Five grams of the compound $C_{22}H_{20}O_7$ was boiled in a flask connected with a reflux condenser with 7 grams caustic potash in 100 cc. methyl alcohol for three hours. The solution was then neutralized, the alcohol distilled off, and the whole acidified and precipitated with water. The precipitate, after being washed and dried, was dissolved in chloroform-ether and extracted with caustic potash. The chloroform-ether solution, on evaporation, yielded a crystalline product which was purified by recrystallizing from alcohol. It separates in very flat plates, having irregular edges (melting-point 136°). Soluble in chloroform, moderately so in alcohol and benzene, and slightly in ether. It is insoluble in caustic potash. It does not take up bromine as does the substance melting at 159°. An attempt was made to convert the substance melting at 159° into this by boiling with the stronger potash solution, but none could be obtained. The pure substance dried at 105° was analyzed with the following results:

I. 0.1666 gram substance gave 0.4073 gram CO_2; and 0.0778 gram H_2O.

II. 0.1646 gram substance gave 0.4001 gram CO_2; and 0.0866 gram H_2O.

	Calculated for $C_{22}H_{20}O_7$.	Found. I.	II.
C	66.66	66.68	66.46
H	5.05	5.19	5.43

A series of molecular weight determinations of the following substances was made in ethylene dibromide:

1. Triphenylmethane; 2. Substance, $C_{23}H_{20}O_7$, melting at 201°; 3. Substance, $C_{22}H_{20}O_8$, melting at 159°; 4. Substance, $C_{22}H_{20}O_7$, melting at 136°.

	Solvent.	Substance.	Δ.	M found.	M (calc.).
I.	26.195	0.1294	0.245	238	244
		0.2747	0.520	238	
II.	23.910	0.1351	0.159	419	408
		0.2491	0.291	423	
III.	27.235	0.2330	0.231	437	412
		0.4127	0.401	446	
IV.	22.885	0.1438	0.178	416	396
		0.2829	0.355	419	

Action of Hydriodic Acid on the Compound $C_{23}H_{20}O_7$.

The substance in question is readily decomposed by hydriodic acid. A determination of methoxy groups was made according to Zeisel's method:

0.3103 gram substance gave 0.3593 gram of silver iodide.

Calculated for two methoxy groups, 0.3566 gram.

The structure, so far as the above experiments go, is therefore represented by $C_{21}H_{16}O_5(OCH_3)_2$.

The substance, in dry chloroform solution, instantly absorbs bromine, and, on evaporation, a crystalline residue can be obtained which is soluble in acetic acid. It melts at 152° to 154° with evolution of hydrobromic acid. It is not affected by alcoholic hydrochloric acid nor by the aqueous acid in sealed tubes at 130°. It does not color ferric chloride solution and is not precipitated by basic lead acetate.

What the relationship is between the compound $C_{23}H_{20}O_7$ and the two compounds produced from it by alcoholic potash, cannot be stated at present; both substances differ from the original only by loss of one carbon atom, and the substance $C_{22}H_{20}O_8$ has also gained oxygen. The quantity of substance obtainable even from a large amount of extract is too small to permit investigation of the products of deep-seated decomposition, so that the future must decide as to the constitution of these interesting compounds, when opportunity comes for obtaining large quantities.

Compound $C_{22}H_{18}O_6$, Melting at 216°.

The crude substance is purified by repeated crystallization

from alcohol. It is obtained in beautiful, fine, yellow needles which dissolve in benzene and chloroform, sparingly in ether and alcohol, and are insoluble in ligroin, insoluble in water or alkaline solution. An analysis of the pure body, dried at 110° gave the following results:

I. 0.1688 gram substance gave 0.4321 gram CO_2; and 0.0751 gram H_2O.

II. 0.1698 gram substance gave 0.4361 gram CO_2; and 0.0746 gram H_2O.

	Calculated for $C_{22}H_{18}O_6$.	Found. I.	II.
C	69.84	69.81	70.05
H	4.76	4.94	4.88

A molecular weight determination was made in naphthalene:

0.1673 gram substance gave Δ 0.227 gram in 14.73 grams solvent.

0.3935 gram substance gave Δ 0.507 gram in 14.73 grams solvent.

1. M = 350; 2. M = 368.

Calculated for $C_{22}H_{18}O_6$: M = 378.

The compound contains two methoxy groups:

0.2816 gram substance gave 0.3536 gram silver iodide.

Calculated for two methoxy groups, 0.3492 gram silver iodide.

The substance therefore has the formula $C_{20}H_{12}O_4(OCH_3)_2$.

In solution in dry chloroform it is slowly affected by bromine, hydrobromic acid being evolved; in moist chloroform bromine is immediately taken up. On adding as much bromine as will be absorbed and then evaporating in a vacuum, a crystalline residue, which can best be recrystallized from benzene, is obtained. It melts at 267° with evolution of hydrobromic acid. The crystals are intensely yellow needles, very soluble in alcohol and ether, sparingly so in alcohol and benzene.

The analysis of this compound shows that it has two bromine atoms in the molecule, but, as, at the same time, a deep-seated change had apparently taken place, the figures do not allow us to express an opinion as to its nature.

The figures obtained for the substance $C_{22}H_{18}O_6$ are very

close to those found by Hart for the so-called piscidine,[1] *i. e.*:

C, 69.78; 69.76; 69.69. H, 4.98 per cent.

Undoubtedly, the substance described as piscidine consists of a mixture of our two substances melting at 216° and 201°, as the melting-point was 192°.

In order to settle this question beyond doubt, we repeated Hart's process, with the result that we obtained the expected mixture, the substance melting at 201° being in large excess. Both substances were identified, after having been separated by the process described above, and as the crystals are very characteristic, there can be no doubt that piscidine really has no existence. Hart's carbon determinations are a little low, a natural result if he had a small amount of the substance melting at 201° in his mixture. Hart assigned the formula $C_{29}H_{24}O_8$ to piscidine. This substance was designated as the active principle of Jamaica dogwood, an assumption for which there is no foundation in fact, as a pharmacological investigation, undertaken by the kindness of Dr. Cushny, demonstrated.

Substance Melting at 50° to 80°.

The crude substance is very soluble in all of the ordinary solvents excepting ligroin, which takes it up only in small quantities. It could not be obtained in a perfectly pure state. When heated with slightly acidified alcohol, it soon deposits crystals of the substance melting at 216°, described above, and the resulting liquid reduces Fehling's solution readily. No other decomposition-product could be isolated, as the alcohol deposited a tar on evaporation. Five grams of the original substance yielded 2.5 grams of the body melting at 216°, after boiling for from five to six hours.

In solution in carbon tetrachloride, the substance decolorizes bromine instantly, with precipitation of the resulting product. This brominated body is insoluble in all ordinary solvents, but it can be purified by recrystallization from amyl alcohol. It melts at 245°. An analysis of this substance probably would clear up the relationship between the substance melting at 50° to 80° and that melting at 216°. Unfor-

[1] This JOURNAL, 8, 9.

tunately, the quantity at our disposal was too small to admit of this investigation. It is probably a glucoside.

Substance Melting at 159° ($C_{25}H_{22}O_7$?).

The body was purified by repeated crystallization from alcohol. Occurring as it does, mixed with the other substances mentioned above, it is very difficult to obtain it in a perfectly pure state. It appears to be in monoclinic crystals, colorless, soluble in chloroform and benzene, sparingly in ether and ligroin; insoluble in aqueous acid or alkaline solution. In pure chloroform solution, it takes up bromine with the formation of a crystalline derivative. An analysis of the pure substance, dried at 105°, gave the following results:

0.1382 gram substance gave 0.3512 gram CO_2; and 0.0691 gram H_2O.

	Found. Per cent.
C	69.18
H	5.26

A molecular weight determination was made in ethylene dibromide.

	Solvent. Grams.	Substance.	Δ.	M.	Calculated for $C_{25}H_{22}O_7$. M.
I	21.6	0.2071	0.274	413	434
II	"	0.3812	0.512	407	

Both the formulas, $C_{15}H_{16}O_5$ and $C_{25}H_{22}O_7$, are in good agreement with the results of the analysis, but the molecular weight determination is in better accord with $C_{25}H_{22}O_7$. The analysis could not be repeated on account of a lack of substance.

Substance Melting at 150° to 155° ($C_{20}H_{22}O_7$).

The crude material was first recrystallized from absolute and then from 70% per cent alcohol, when it formed small, needle-shaped, colorless crystals, melting at 150° to 155° with decomposition and evolution of a gas. The substance is very soluble in ethyl or methyl alcohol, moderately so in acetone, and is sparingly dissolved by ether, chloroform, benzene, or hot water. It is insoluble in ligroin. It is readily taken up by hot alkalies, either caustic or carbonates, and is then colored red. The alcoholic solution becomes brown on stand-

ing, the chloroform solution blue; and when an attempt was made to dry the crystals at 100° they darkened materially. The substance reduces Fehling's solution and ammoniacal silver nitrate. Dissolved in alcohol it even blackens neutral silver nitrate. The body gives a green color with ferric chloride and is neutral.

Crystals dried *in vacuo* over sulphuric acid gave the following analytical results:

I. 0.1585 gram substance gave 0.3731 gram CO_2; and 0.0859 gram H_2O.

II. 0.1722 gram substance gave 0.4040 gram CO_2; and 0.0897 gram H_2O.

III. 0.1786 gram substance gave 0.4209 gram CO_2; and 0.0952 gram H_2O.

	Calculated for $C_{20}H_{22}O_7$.	Found. I.	II.	III.
C	64.17	64.20	64.08	64.27
H	5.88	6.02	5.79	5.92

The sample used in the third analysis was different from the other two.

A molecular weight determination was made in phenol.

Solvent. Grams.	Substance.	Δ.	M.
16.956	0.347	0.62	231

The result would make a formula (1) $C_{11}H_{10}O_4$ (C = 64.08, H = 4.85) the more probable one, but from considerations to be advanced below, there can be no question that the one given above (2) is correct. The solvent therefore has a partial dissociating action on the solute. Two other formulas, *viz.*, (3) $C_{17}H_{18}O_6$ and (4) $C_{23}H_{26}O_8$, are also in close agreement with the analytical numbers, but these must also be abandoned for similar reasons.

Action of Acids on the Substance $C_{20}H_{22}O_7$.

When heated with slightly acidified alcohol the compound is decomposed, and a much less soluble substance is precipitated, the same effect being produced by strong sulphuric acid. The latter method gives the best results.

Two grams of the shbstance $C_{20}H_{22}O_7$ were dissolved in concentrated sulphuric acid (2 parts acid to 1 part water) at

about 50°. Solution immediately took place, a greenish-yellow color appeared and the temperature of the mixture rose. No odor was emitted, and no gas given off. The solution was then precipitated with water, filtered, and washed with water and dried (weight 1.8 grams). The crude substance was then recrystallized from glacial acetic acid and finally from alcohol.

The pure crystals are colorless and appear in the form of rectangular plates, melting at 275°, with slight coloration. They are moderately soluble in acetone, sparingly so in acetic acid, and almost insoluble in ethyl or methyl alcohol, ether, benzene, or chloroform. They are readily taken up by caustic potash or sodium carbonate on warming. They do not reduce either Fehling's solution or ammoniacal silver nitrate, even on warming, and they color alcoholic ferric chloride green.

I. 0.1512 gram substance gave 0.3643 gram CO_2; and 0.0699 gram H_2O.

II. 0.1375 gram substance gave 0.3329 gram CO_2; and 0.0655 gram H_2O.

III. 0.1569 gram substance gave 0.3811 gram CO_2; and 0.0762 gram H_2O.

IV. 0.1537 gram substance gave 0.3713 gram CO_2; and 0.0743 gram H_2O.

	Found.			
	I.	II.	III.	IV.
C	65.71	66.02	66.24	65.88
H	5.19	5.37	5.39	5.37

Calculated for I. $C_{18}H_{16}O_6$: C, 65.85; H, 4.88; M, 328.
II. $C_{21}H_{20}O_7$: C, 65.63; H, 5.21; M, 384.
III. $C_{15}H_{14}O_5$: C, 65.69; H, 5.11; M, 274.

A molecular weight determination in phenol gave :

Solvent.	Substance.	Δ.	M.
14.543	0.2109	0.365	286

Formulas (1) and (2) result from formulas (3) and (4) (given above), respectively, by separation of alcohol.

$$C_{20}H_{22}O_7 = C_{18}H_{16}O_6 + C_2H_6O;$$
$$C_{23}H_{26}O_8 = C_{21}H_{20}O_7 + C_2H_6O.$$

The filtrate from the preparation of the substance melting at 275° was, therefore, subjected to fractional distillation in the hope of detecting the presence of alcohol. The first fraction which passed over was tested with iodine and alkali, and a decided iodoform reaction was obtained. It did not reduce ammoniacal silver nitrate. The molecular weight agrees best with $C_{15}H_{14}O_5$, but by reason of results obtained by acetylation, this is not possible, so that here also the phenol has a dissociating effect as a solvent.

Acetylation of the Compound $C_{20}H_{22}O_7$.

When treated in the usual way with sodium acetate and acetic anhydride, the body readily yields an acetyl derivative in colorless crystals, melting at 183°. The substance is boiled for several hours in connection with a reflux condenser with 10 parts of acetic anhydride and 3 parts of sodium acetate. After cooling and pouring into water, it solidifies. It is filtered, washed with water, and recrystallized from alcohol to which a little animal charcoal has been added. The yield is apparently quantitative, and the body is pure after the first recrystallization. The body dried at 105° gave the following numbers:

I. 0.1462 gram substance gave 0.3361 gram CO_2; and 0.0684 gram H_2O.

II. 0.2112 gram substance gave 0.4872 gram CO_2; and 0.1005 gram H_2O.

Calculated for triacetyl derivative, $C_{26}H_{28}O_{10}$: C, 62.4; H, 5.6.

Calculated for diacetyl derivative, $C_{24}H_{26}O_9$: C, 62.88; H, 5.68.

	Found.	
	I.	II.
C	62.70	62.91
H	5.19	5.28

A molecular weight determination made in benzene gave:

Solvent. Grams.	Substance.	Δ.	M.
11.275	0.1895	0.171	491
"	0.4112	0.358	509

Calculated for $C_{24}H_{26}O_9$: M = 458.

On treating this acetyl derivative with sulphuric acid (5 parts acid to 2 parts water) it is dissolved on warming, and acetic acid is liberated. After heating in this way for two hours the product was diluted with water and a precipitate which formed filtered. This substance proved to be the decomposition-product, melting at 275°, described above, so that sulphuric acid splits off alcohol as well as acetic acid. As the compound melting at 275° is quite stable in the presence of sulphuric acid, an attempt was made to determine the number of acetyl groups present in the acetylation-products in this way.

0.5009 gram substance was dissolved in 12 grams of sulphuric acid (5 parts acid to 1 part water), and after heating on the water-bath for one hour was precipitated with 150 grams of water, then digested on a water-bath for a few minutes, allowed to cool, the residue filtered, washed, and weighed. Total, 0.3407 gram. The solubility of the same quantity of pure substance in the same amount of solvent is 2.9 per cent. Applying this correction, we have 0.351 gram, or 70.71 per cent of the original substance.

Calculated for $C_{18}H_{16}O_6$ from $C_{34}H_{36}O_9 = 71.6$ per cent.

A second experiment gave 69.5 per cent.

While this method is not suitable for exact quantitative work, it is nevertheless sufficiently accurate to show conclusively that the body is a diacetyl derivative.

Acetylation of the Substance Melting at 275° ($C_{18}H_{16}O_6$).

When treated in the same way as the compound melting at 150° to 155°, an acetyl derivative, separating from alcohol in crystals resembling calcite, melting at 177° to 178°, when in the pure state, is obtained.

I. 0.2184 gram substance gave 0.5089 gram CO_2; and 0.1025 gram H_2O.

II. 0.1660 gram substance gave 0.3899 gram CO_2; and 0.0755 gram H_2O.

III. 0.1518 gram substance gave 0.3560 gram CO_2; and 0.0717 gram H_2O.

	Found.		
	I.	II.	III.
C	63.55	64.06	63.96
H	5.21	5.19	5.25

A molecular weight determination was made in benzene:

Solvent. Grams.	Substance.	Δ.	M.
11.58	0.1488	0.149	419
"	0.3022	0.280	466

Calculated for $C_{22}H_{20}O_8$ (diacetyl derivative): C, 64.08; H, 4.85; M, 412.

This substance is therefore a diacetyl derivative of the compound $C_{18}H_{16}O_6$, so that the separation of alcohol from the compound $C_{20}H_{22}O_7$ has not produced an additional alcoholic hydroxyl group.

The acetyl derivative dissolves in dilute sulphuric acid (2 parts acid to 5 parts water) with liberation of acetic acid. In this case, however, the sulphuric acid caused a certain amount of decomposition, so that an attempt to determine the number of acetyl groups as in the previous case resulted in numbers which fell between those calculated for two and for three groups, although nearer to the former. The precipitated body could not be obtained in a crystalline state.

Other Reactions of the Compound $C_{20}H_{22}O_7$.

The substance is quite readily decomposed by caustic potash and by means of a mixture of this and methyl iodide, a new body could be obtained.

The compound $C_{20}H_{22}O_7$ was dissolved in a small amount of a solution of caustic potash and then boiled on the water-bath with an excess of methyl iodide in methyl alcohol, small pieces of potash being added from time to time as the substance became neutral. The solvent was then evaporated, and the alkaline solution extracted with ether. On evaporating the ether, there remained a crystalline body, separating from methyl or dilute ethyl alcohol in needles, insoluble in petroleum ether; melting-point 141° to 142°. Only enough substance remained for two analyses, which did not agree closely, but the numbers come closest to those calculated for a dimethyl derivative of the substance $C_{18}H_{16}O_6$ (melting-point 275°).

(Calculated: carbon, 67.41, hydrogen 5.6; Found: carbon 67.90, hydrogen 6.47).

The formula given for $C_{20}H_{22}O_7$ and its derivatives must be regarded as the most probable, but other series may be shown to agree with the results tolerably well. The molecular weight determinations were all more or less unsatisfactory owing to the high numbers, the acetyl derivatives did not yield entirely reliable results, and combustions of substances with such high molecular weights of necessity allow more than one interpretation, so the final disposition of the problem must be left for a time when, with larger quantities of material, sufficiently large amounts of methyl derivatives can be obtained to settle the question by a quantitative estimation of methoxy groups.

The bodies obtained from Jamaica dogwood, and so far as we know, the only ones present in this substance, are given in the following table :

Substance.	Formula.	Melting-point.
Piscidic acid	$C_{11}H_{12}O_7$	185°
Ethyl ester	$C_{13}H_{16}O_7$	207°
Anilide	$C_{28}H_{22}N_2O_5$	196°
Acetyl derivative	$C_{17}H_{20}O_9$	149°
Bromine "	$C_{11}H_{13}O_7Br_2$(?)	234°
Neutral solution.		
First body	$C_{23}H_{20}O_7$	201°, contains 2 methoxy groups
Decomposition-product of above	$C_{22}H_{20}O_8$	159°
Decomposition-product of above	$C_{22}H_{20}O_7$	136°
Second body	$C_{24}H_{16}O_6$	216°, contains two methoxy groups
Third "		50° to 80°
Fourth "	$C_{23}H_{22}O_7$(?)	159°
Fifth "	$C_{20}H_{22}O_7$	150° to 155°
Decomposition-product	$C_{18}H_{16}O_6$	275°
Acetyl derivative	$C_{24}H_{20}O_9$	183°
Acetyl derivative of 275° body	$C_{22}H_{20}O_8$	177°
Methyl iodide derivative	$C_{30}H_{20}O_6$(?)	141°

The present work has demonstrated the large number of interesting crystalline derivatives to be found in Jamaica dogwood, and it has given means for their isolation, together

with some facts which show the direction which investigation must take in determining the constitution of the substances in question.

Scarcely any plant product shows so great a diversity of bodies, and a series, the members of which evidently are so closely related. The subject of the constitution of these bodies and their interrelationship will, in the future, form a most interesting chapter in plant chemistry. The investigation will have to be carried on with large quantities of the bark, not less than 400 or 500 pounds. At present the work must stand as it is, but we soon hope to be able again to take up the investigation of the structure of piscidic acid, of which larger quantities than of the other derivatives can be obtained.

ANN ARBOR, October, 1900.

THE CRYSTALLIZATION OF COPPER SULPHATE.

BY ARTHUR JOHN HOPKINS.

The Size of Crystals.

The work described in this paper had for its object the preparation of crystals of copper sulphate, which should be from 20 to 30 mm. in length. The first part contains a short discussion of those general conditions which determine the size of crystals, together with a development of a method for the preparation of crystals of any desired size. The following principles guided the work:

I. In the process of crystallizing copper sulphate, at constant room temperature, the solubility is a constant and the concentration (weight of solute in unit volume) minus this constant is the total weight of crystal deposit. Or, in other words, in the process of crystallizing copper sulphate at constant room temperature, the concentration determines the weight of the crystal deposit.

II. (*a*) In a solution, supersaturated in absolute quiet, no crystals will form.

(*b*) In a solution supersaturated in absolute quiet, the number of crystal points formed by the first disturbance (if the disturbance is succeeded by quiet) is the same as the number of crystals finally formed.

(*c*) The ratio between the number of crystals formed and the weight of crystal deposit determines the size of the crystals.

III. For a given volume of solution and given size of crystals and weight of crystal deposit, the diameter of the crystallizing dish determines the space between the crystals.

The usual laboratory practice of preparing a solution of known concentration with the expectation of getting crystals of definite size is therefore misleading, as this method gives only one definite result, *i. e.*, a certain weight of crystal deposit, as is expressed by the first principle. From principle II. it is clear that the number of crystals to be formed is determined almost instantaneously, *i. e.*, that nothing in the previous history of the solution (its concentration, the size of the dish, or the rate of cooling) directly determines the number of crystals, but that as the solution cools beyond the point of saturation, a few crystal points suddenly started, whether by direction or accidentally, will slowly grow by addition from the solution and, if given equal opportunity, will grow equally, each crystal's final weight becoming the quotient of the total weight of crystals deposited, divided by the number of points started.

Again, from the third principle, it is evidently desirable that the dish be large enough to allow the crystals full room to grow without crowding.

The experiments of the two parts of this paper number about 60. The first experiments are passed over. They proved that neither concentration alone, nor the relation of the size of the dish to the volume of the solution nor the rapidity of cooling determines the size of the crystals. These facts were all proved later by two experiments, as follows: First, bring a solution of definite volume and concentration to supersaturation in absolute quiet and then, after disturbing, note the size of crystals formed. Second, after warming the crystals and the solution obtained as described, repeat the first experiment, when crystals of an entirely different size will probably be deposited. A single such experiment shows that the slightest accident, after saturation, may determine the size of crystals.

In all of this work, dust was excluded as rigorously as possible by careful filtering of solutions and scrupulous cleaning of crystallizing and other dishes. In order to prevent carbonate from forming and acting as centers of crystallization, recently boiled water was used at first, then water known to be free from carbonic acid, but finally it was found necessary (in continued crystallizations of the same solution) to add about 5 cc. of normal sulphuric acid to every 100 cc. of solution. Uniformity in measuring (without danger of error due to contraction on cooling to indefinite degrees) was approximated by concentrating the filtered and perfectly clear solution in a marked beaker to a volume smaller than that desired, pouring quickly into a hot measuring cylinder, transferring the last drops by aid of a little boiling water, filling the cylinder to the desired volume with boiling water, and pouring the solution quickly into a clean crystallizing dish, which was immediately covered. All of these experiments were conducted in a room held at constant temperature by a heat regulator, and a watch was kept on the indications of a maximum and minimum thermometer. A variation of 2° was unusual and occurred only during the night.

Experiments showed that solutions of convenient concentration and volume were obtained, when 171 grams of clean copper sulphate crystals were dissolved in water and 15 cc. of normal sulphuric acid were added, and the whole was concentrated to less than 340 cc. and diluted to exactly that volume with boiling water, the volume being read when the solution was as near as possible at boiling temperature. All the solutions were started in this way, and all solutions, not of the same volume, were of this concentration. The size of the crystals decided upon as desirable for quantitative work was a length varying from 20 to 30 mm. The ratio of the volume of solution to the horizontal surface of the containing crystallizing dish is identical with the depth of solution, and so for each volume a dish was selected which would give a constant depth. A depth of about 6 mm. was found to give ample space between crystals 20 to 30 mm. long, formed from a solution of the strength indicated; and in so shallow a solution there is the added advantage that the crystals, when first

formed on the surface, fall to the bottom directly without slant. The diameter of the dish, which will hold 340 cc. at a depth of 6.3 mm., is 26 cm., and, in general, the diameter for this depth is the square root of twice the contained volume.

From the previous discussion it will be seen that with a given volume and concentration and with the size of the dish determined, the size of the crystals will depend upon the number of crystal points first started in the solution as it cools beyond the point of saturation, and that the number of these points depends upon the conditions which obtain in the crystallizing dish during the time of supersaturation, and only then. Of course one can escape the uncertainty of accident by providing in such a solution a sufficient number of minute, clean crystals to supply nuclei for crystallization, but these should be so small as not materially to increase the concentration. A difficulty would arise in this method of procedure in that the temperature would have to be chosen so low that the little crystals would not dissolve in the hot solution before growth began, and also so high that the cold crystals would not locally chill the surface of the solution below the saturation-point and thus start crystallization in a fine powder throughout the whole mass. For the volume and concentration above indicated, about fifty such points would be necessary to give crystals of 30 mm. in length.

The method used in this work for starting the proper number of crystal points is one which, with a little practice on the part of the experimenter, works satisfactorily—how much so will be seen from the second part of this paper. When the hot measured solution is poured into the crystallizing dish, the latter is carefully covered to prevent further concentration, dust or surface chilling, and is allowed from eight to ten minutes to cool, when a slight blast of air (the air being filtered through cotton) under pressure equivalent to 12 mm. of mercury is blown upon the surface, and the latter is watched closely for the first minute crystals which (formed before the colder blast) float out upon the surface. When the proper number of these crystals for the volume and concentration are not only formed but persist in the hot solution, the blast is quickly removed, and the crystals are al-

lowed to grow while the dish is covered and left undisturbed at constant temperature, usually over night. As the number of crystals always bears the same relation to the surface exposed, one watches not for a certain number of crystals but rather for a certain spacing, constant for each experiment, which it is easy to approximate each time.

Successive Crystallizations.

In the experiments mentioned above, 171 grams of clean copper sulphate crystals were dissolved in acidified water and concentrated to 340 cc. On crystallization at 23° (C.), 275 cc. of mother-liquor and 78 grams of crystals were obtained. It was desired to evaporate further the 275 cc. of concentrated solution to the same strength as the 340 cc. of the original solution—a concentration which will always give the ratio of 78 grams of crystals to 275 cc. of mother-liquor. It was calculated[1] that to this end any saturated solution of copper sulphate must be evaporated to 67.1 per cent of its volume, and that this will then give a mother-liquor equal to 54.3 per cent and a crystal weight equal to 15.4 per cent of the same volume.

Based upon this calculation, a model has been constructed which is found in Table I., below. According to this table, each mother-liquor is to be concentrated to 67.1 per cent of its volume, and from it is to be obtained a weight of crystals and a volume of new mother-liquor in the ratio of 28+ grams to 100 cc. Table II. contains the results of the first attempt to follow this model. By comparing these tables, it will be seen that the point of concentration indicated in the second column of Table I. was not reached exactly in any case but the important column VI. of Table II. shows that the size of crystals has fallen each time within the desired limits of from 20 to 30 mm. in length.

[1] The calculation is as follows:

275 : 78 = 100 : 28.3.

Solubility at 23° = 21.7 grams $CuSO_4$, sp. gr. of solution being 1.21+.

21.7 grams $CuSO_4$ = 33.8 grams $CuSO_4.5H_2O$.

Required: 0.338 V − 0.338 V' = 0.283 V', or mother-liquor, V', = 54.3 per cent V.

Then the original solution at point of saturation at 23° must have measured 275 + 0.543 = 506.4 cc.

340 ÷ 506.4 = 67.1 per cent, evaporating ratio.

0.284 × 0.543 = 15.4 per cent, ratio of crystal weight to saturated solution.

Table I. Model.

Process number.	I. Solution saturated at 25°. Each volume = 54.3 per cent of preceding. cc.	II. Solution evaporated to 67.1 per cent of volume in I. cc.	III. Weight of crystals = 15.4 per cent of volume in I.	IV. Ratio of weight of crystals to volume in I.	V. Diameter of crystallizing dish to give solution in II. a depth of 6+ mm. $D = \sqrt{2}.V.$	VI. Size of crystals.
1	[506.4 calculated]	340			$\sqrt{680} =$	
	275		78	0.283	26	
2	275	184			$\sqrt{369} =$	
	149		42	0.282	19	
3	149	100			$\sqrt{200} =$	
	81		23	0.284	14	
4	81	54			$\sqrt{109} =$	
	44		12.5	0.284	10.5	

Table II.

	I.	II.	III.	IV.	V.	VI.
1	x	340				
	275		78	0.283	25	20
2	275	190				
	157		39	0.248	20	20
3	157	105				
	85		25	0.294	13.5	26
4	85	58				
	50		12+	0.24	9.6	26

It should be said concerning the figures in columns I. to IV. that it is very difficult to measure quickly solutions which are held as closely as possible to the boiling temperature, and that an approximation to the model was all that was necessary, since large variations do not appreciably affect the results in column VI., which contains the results especially sought.

When the solution gets as small as 58 cc., the nuclei may be supplied by introducing minute crystals—as only ten are needed in this case—but these crystals must first be washed with hot water and must then be large enough to exist in the hot solution. In larger solutions the method described is better.

Should one desire to form crystals of a different size, a little practice would be necessary to determine the proper condition of spacing for that size, and the formula for the size of the crystallizing dish would be somewhat changed. It would then be possible to prepare crystals of any desired size not only from the original solution but from all the successive mother-liquors.

AMHERST COLLEGE, September, 1900.

ON METHYL CYANIDE AS A CATALYTIC REAGENT; AND A CRITICISM OF J. U. NEF'S VIEWS ON THE FRANKLAND, WURTZ, AND CONRAD REACTIONS.

BY ARTHUR MICHAEL.

In the Wurtz sodium method for preparing alkanes it has been found necessary, in some cases, to heat the ingredients in a closed tube; an operation that not alone greatly increases the difficulty of preparation, but also, usually, materially decreases the yield of hydrocarbon obtained. Several chemicals, like ether and acetic ester, have been found to facilitate the reaction with certain iodides, but I have failed to notice any decided influence in some other instances, which have come under my notice. A number of other organic substances were examined, and in methyl cyanide the catalytic property was noticed to be developed to a very considerable degree. I was intended to investigate this interesting subject more caretfully, but as several years have already passed and I have been unable to do so on account of other more pressing work, these incomplete observations are communicated, in the hope that this new catalytic reagent may prove of service to chemists who are now working in this field.

The behavior of methyl iodide towards sodium was examined by Buckeisen and Wanklyn,[1] who heated these substances and ether in a sealed tube to 100° and obtained ethane, mixed, however, with methane in considerably larger proportion, and a small amount of ethylene. Sodium wire does not react with dry methyl iodide, even after standing some hours

[1] Ann. Chem. (Liebig), 116, 329.

at room temperature, but if the mixture is well cooled in ice-water, and a drop or two of methyl cyanide added, an energetic reaction soon takes place, with formation of a permanent gas that, to judge from the color of its flame, could have hardly contained an appreciable proportion of ethylene.

The behavior of ethyl iodide towards sodium has not been examined, although Löwig[1] has described the formation of normal butane by the action of sodium amalgam. Sodium wire and ethyl iodide react very slowly and imperfectly at ordinary temperature, but the addition of a drop or two of acetonitrile soon causes, according to the dilution of the cyanide, a reaction, which, if not moderated by cooling, may become very violent. To prepare butane by this method it is advisable to connect the lateral tube of a fractionating flask with a condenser and its neck with a dropping-funnel, and, after introducing the sodium wire and some dry ethyl iodide into the flask, to displace the air by a current of carbon dioxide. Several drops of acetonitrile are then added, and the reaction kept in moderation by sufficient cooling, adding from time to time more iodide, which may contain a very small amount of the nitrile. A good yield of butane is obtained in this way, which may contain some ethane and ethylene, but, if present at all, they certainly are in much smaller proportion than when butane is prepared by the Frankland method.

Normal hexane was prepared by Schorlemmer,[2] who found that sodium does not react on propyl iodide in presence of ether, even on boiling the mixture, and obtained the hydrocarbon by heating the iodide and metal in a sealed tube to 150°. If several drops of acetonitrile[3] are added to sodium wire, covered by propyl iodide, a reaction is immediately noticeable, and, if the dilution is not very great, the mixture soon begins to boil, and cooling becomes necessary; thus, two drops of the nitrile added to 10 grams propyl iodide and the equivalent amount of sodium, caused a violent reaction in a few minutes, while at five times this dilution the reaction proceeds

[1] J. prakt. Chem., **79**, 441.

[2] Ann. Chem. (Liebig), **161**, 277.

[3] According to Stohman and Kleber (J. prakt. Chem., [2], **43**, 7) freshly pressed sodium wire reacts at once on propyl iodide, but, although this experiment was repeated several times, we never noticed a reaction until the nitrile was added.

gently, under slight warming, and continues for about twelve hours; in either case a small quantity of iodide remained unconverted. In an experiment with 310 grams of propyl iodide, with 10 per cent excess of sodium wire, in a flask connected with a return condenser, 5 drops of cyanide were added, and the mixture allowed to stand for a day. Then it was heated on a water-bath for several hours, and the hydrocarbon distilled off. The hexane thus obtained was heated to 100° in a sealed tube, with a little sodium, for eight hours, and, after fractionation, was found to be pure. The yield was 80 per cent of the theory, which probably could have been somewhat increased by very careful handling of this volatile hydrocarbon.[1]

The following experiments should be considered as preliminary tests:

Allyl iodide and sodium, according to Berthelot and Luca,[2] react on heating to form diallyl, but it is not necessary to heat the mixture, although at room temperature the reaction proceeds very slowly. Addition of several drops of acetonitrile soon induces a violent reaction, which it is well to moderate by cooling in ice-water, with formation of diallyl, apparently with a good yield.

Isopropyl iodide and sodium wire did not react, but on addition of a little nitrile, a decomposition occurred after the mixture had stood about half an hour.

Trimethylene bromide was only very slowly decomposed by sodium, which at first was not increased by addition of the nitrile, but after about twenty minutes a rapid reaction took place, with evolution of gas.

Benzyl chloride reacts slowly with sodium wire at ordinary temperature, and the preparation of dibenzyl is effected by heating the mixture.[3] Addition of acetonitrile soon induces a reaction, which proceeds rapidly, unless the mixture is cooled. The yield of dibenzyl, according to this method, is greater than when sodium is used alone at a higher temperature, as less by-products are formed.

This catalytic property of methyl cyanide is shared by ethyl

[1] The experiments with propyl iodide were done with W. W. Garner.

[2] Ann. chim. phys., [3], **48**, 294.

[3] Ann. Chem. (Liebig), **121**, 250; *Ibid.*, **137**, 258.

and propyl cyanides, although, particularly in the case of the last substance, the inductive capacity appears to be less developed, and with aromatic cyanides, benzonitrile and benzyl cyanide, no acceleration of the reaction was noticed. It would seem that these conditions indicate an influence of the fatty cyanides, which is not dependent on the action of the metal on them, as benzonitrile, which does not act as an inducer, is also attacked by sodium.

In connection with a research on the action of zinc ethyl iodide and zinc ethyl on unsaturated α,β-esters[1] several experiments were made, which gave results connected with the inducing properties of esters on the action of zinc on ethyl iodide, and these will be mentioned in this note.

It is a well known fact that ethyl iodide reacts but slowly on zinc, even when heated with it, and that the formation of zinc ethyl iodide may be greatly facilitated by the addition of ether or acetic ester. The following experiment indicates that oxalic ester can also act as an inducer. Ten grams of dry ethylene bromide (dried over phosphorus pentoxide) and 5 grams freshly pulverized zinc-sodium were heated, first to 100°, then, as no action took place, to boiling; but even at that temperature only a very slight evolution of a gas was noticed. The mixture was then cooled and 8 grams of dry oxalic ester added, when, on heating to about 40° C., a vigorous evolution of a gas occurred, which burnt with an almost colorless flame. After the reaction moderated it was completed by heating the flask for some hours to 100°, which was then heated, connected with an inverted condenser, in a salt-water bath as long as an oil passed over. In this way 3 grams of oil were obtained, which boiled almost entirely at 39°, and consisted of ethyl bromide:

0.1363 gram oil gave 0.2341 gram AgBr.

	Calculated for C_2H_5Br.	Found.
Br	73.3	73.1

The inducing influence of ether in the preparation of zinc ethyl was first noticed by Frankland, and later Pebal[2] based a

[1] Michael: Ber. d. chem. Ges., **20**, 1791; J. prakt. Chem. (N. F.), **60**, 477. The details of this work will be published later.

[2] Ann. Chem. (Liebig), **118**, 22.

method for obtaining that substance in an open vessel on this observation. If zinc and ethyl iodide, in equivalent proportions, in a flask connected with an inverted condenser, are mixed with an equal volume of dry ether, and, after driving out the air in the apparatus by carbon dioxide, are heated on a water-bath, the zinc is gradually used up, without evolution of gas in a considerable proportion. The ether contains a good yield of zinc ethyl iodide, which is left as large, white crystals when the solvent is driven off. It seems to have been overlooked that this substance may be used in many of the preparations, which involve the use of zinc ethyl, and the synthesis of ethylphenylketone is given as an example of the method. Twenty-five grams of ethyl iodide were converted into zinc ethyl iodide, the solution cooled in ice-water, and 22.5 grams benzoyl chloride, diluted with twice its volume of dry ether, gradually added. The reaction proceeded in the cold, and next morning all the chloride had disappeared. The contents of the flask were thrown on broken ice, then acidified thoroughly, shaken, and the ether separated and extracted with caustic soda. On fractionation of this ethereal solution about 30 per cent of ethylphenylketone was obtained, besides 4 grams of product boiling from 193°–196° under 9 mm. and a little of a white crystalline substance, neither of which bodies was further examined. A better yield of diethyl ketone was obtained by using this method, and it seems likely that, if the exact amount of zinc ethyl iodide formed from a given weight of ethyl iodide were ascertained, the process might advantageously replace that which involves the use of zinc ethyl in many synthetical reactions.

The action of zinc on a mixture of ethyl iodide and malonic ester has been investigated by Daimler,[1] who found that, on warming the mixture, ethane is given off and ethyl malonic ester is formed. According to the interpretation of this interesting synthesis given by the discoverer, the metal probably works indirectly, first acting on the ethyl iodide. Daimler only mentioned this construction of the reaction, leaving the details and further procedure an open question, but the following experiments show that the reaction

[1] Ann. Chem. (Liebig), 249, 173.

proceeds with the formation of zinc ethyl iodide, which, reacting with malonic ester, yields a metallic derivative, and that the further action of ethyl iodide on this product proceeds with formation of ethyl malonic ester and zinc iodide. Twenty-five grams of ethyl iodide were converted into zinc ethyl iodide, and 24.5 grams of malonic ester were slowly added to the ethereal solution, cooling, when necessary, to avoid a violent reaction. During the operation a gas came off abundantly, which burnt with a pale flame and evidently consisted of ethane. After standing twelve hours,[1] 24 grams of ethyl iodide were added, and the mixture boiled four hours. On adding the product to ice-water no gas was evolved, and the ether solution, after drying, gave, on fractionation, the following result:

		Grams.
I.	205° –208°.5	0.8
II.	208°.5–214°	18.0
III.	214° –217°	3.0

On refractionating II. and III. several times with beads, 12 grams of oil boiling from 209°.5 to 211°.5 were obtained, which consisted of pure ethyl malonic ester, and 8 grams oil boiling from 211°.5 to 217°, probably mostly ethyl—with some diethyl malonic ester. An analysis of the portion boiling from 209°.5-211°.5 gave the following result:

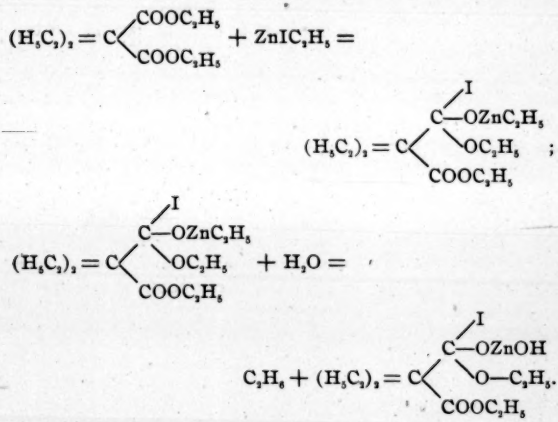
0.1582 gram of oil gave 0.3340 gram CO_2; and 0.1224 gram H_2O.

	Calculated for $C_9H_{16}O_4$.	Found.
C	57.4	57.6
H	8.5	8.6

Diethyl malonic ester acts, as a neutral body towards sodium, and the following experiment showing, not alone the inductive influence of the ester in forming zinc ethyl iodide, but also that it may form a metallic derivative, is not without theoretical interest. Five grams ester, 3.5 of zinc, and 8.3 of ethyl iodide were heated, under a pressure of 100 mm., for twelve hours, when almost all the zinc had disappeared. The evolution of gas during this operation was comparatively slight. The ethereal solution was thrown into

[1] If this product is thrown into acidulated water, malonic ester is regenerated.

250 cc. cold water, when considerable ethane was given off, the liquid well shaken, and the voluminous precipitate filtered under pressure, washed, and well pressed between filter-paper. This precipitate contained zinc and iodine, and after decomposition by an acid, gave 3.2 grams of an oil, which boiled from 223° to 228° (corr.), and consisted largely of unchanged diethyl malonic ester. A possible interpretation of this behavior may be represented by the following equations:



In a recent paper[1] J. U. Nef has treated the formation of ethyl malonic ester by means of zinc, as well as the Frankland, Wurtz, and Conrad syntheses, from a peculiar point of view. These conceptions of Nef's arise from an imperfect understanding of the fundamental chemical processes, particularly that of the relations of elimination and addition to chemical structure and to each other, and in misunderstanding[2] the conditions that lead to the formation and existence of divalent carbon. I have already shown[3] such a criticism of a portion of Nef's paper, to be well founded, and it is not difficult to prove that his interpre-

[1] Ann. Chem. (Liebig), **298**, 202.
[2] Michael: J. prakt. Chem. (N. F.), **60**, 478.
[3] *Ibid.*, **60**, 471.

tation of the Frankland, Wurtz, and Conrad reactions is open to the same objections. The idea that some reactions, which apparently have gone by substitution are, in reality, the result of an eliminative process, followed by that of an additive, inasmuch as the unsaturated body first formed passes over, by addition of one of the reagents used or of a substance formed in the reaction, into a saturated compound, is by no means as new as Nef supposes. It was discussed by Linnemann[1] in his papers on the direct conversion of certain primary propyl and isobutyl derivatives into corresponding secondary and tertiary products; and this explanation was considered by V. Meyer[2] as a satisfactory explanation for some of these abnormal reactions. Tscherniak[3] assumed that the appearance of nitrous esters in the action of ethyl iodide and its homologues on silver nitrite is due to the formation of alkylenes, which unite with the nitrous acid formed in the reaction; but later, Meyer[4] showed that propyl and isopropyl iodides give isomeric nitrites, whereas, if their formation were due to the intermediate formation of propylene, isopropyl nitrite alone should be generated. Linnemann[5] returned to this method of explanation, and, as he proved that propylene bromide with zinc and water at 100°, *i. e.*, nascent propylene, does not form isopropyl addition alcohol, he considered the addition hypothesis inadequate.[6]

The first experimental proof that elimination may precede substitution was given by the writer,[7] who showed that α,β-dibrompropionic ester and α-bromacrylic ester in their reaction with sodium malonic ester give the same product, an observation which led to the discovery of the property of α,β-unsaturated esters and ketones to give addition-products with such sodium derivatives.[8]

[1] Ann. Chem. (Liebig), **161**, 53; **162**, 29.
[2] Ber. d. chem. Ges., **9**, 539, 535; **10**, 130.
[3] Ann. Chem. (Liebig), **180**, 157.
[4] Ber. d. chem. Ges., **9**, 534.
[5] *Loc. cit.*, **10**, 1111.
[6] The conditions in these experiments and in those of nitrous acid on propylamine are not strictly comparable, as the presence of an acid materially facilitates the addition of water. However, there is as yet no proof that the formation of secondary propyl alcohol in the latter instance results from that of propylene.
[7] J. prakt. Chem., (2), **35**, 132.
[8] *Loc. cit.*, 349. It may be observed that the short account given above by no means represents the complete literature on this subject.

It was especially emphasized[1] at the time that, when elimination proceeds very easily, as is the case with α,β-dibrompropionic ester, and when under the observed conditions the unsaturated derivative thus formed can unite with the other reagent, it is absolutely necessary to take the possibility of the reaction going in this way into consideration. The experience of Bischoff[2] and Auwers and Jackson[3] several years later, in the study of the action of sodium malonic ester on α-bromisobutyric ester tended to confirm the necessity of determining the relations of eliminative and substitutive processes to chemical structure. In recent years, several other reactions bearing on this subject have been carefully studied, and I have been able to prove, step by step, that such eliminative and subsequent addition processes really occur, as well as to connect the relations between them and substitution with the chemical structure of the substance, so that we now know, in most cases, when we may expect one or the other decomposition, or a mixed reaction, resulting from a simultaneous procedure in both directions.[4]

It is interesting to note the changes in the elimination and addition theory that have been suggested by Nef, and for our purpose it will suffice to discuss the behavior of propyl iodide and isopropyl iodide to obtain a proper appreciation of his ideas. Nef[5] starts with the assumption that malonic ester is a perfectly neutral compound, an assumption that is based on some inaccurate observations of his own.[6] He then concludes that because sodium malonic ester is decomposed by water it must also undergo a like decomposition to a great extent by absolute alcohol, which represents such an obviously wrong assumption that it is not necessary to discuss it. The next step assumes the dissociation of the iodides by sodium ethylate into propylene and hydriodic acid, and that the free malonic ester present, or that formed by the acid reacting on sodium malonic ester, then adds to the nascent propylene to form propyl ma-

[1] *Loc. cit.*, 356.

[2] Ber. d. chem. Ges., **23**, 1464.

[3] *Loc. cit.*, 1599.

[4] Ber. d. chem. Ges., **28**, 2512; **29**, 1792. J. prakt. Chem., (N. F.), **60**, 372–384 409–420.

[5] Ann. Chem. (Liebig), **298**, 262.

[6] Ann. Chem. (Liebig), **266**, 67; Compare Michael: J. prakt. Chem., [2], **46**, 194; Conrad and Gast: Ber. d. chem. Ges., **31**, 1339; Willstätter: *Loc. cit.*, **32**, 3276.

lonic ester. These assumptions complete the chain of impossible conceptions, for, not only can we perform the same reactions with sodium malonic ester that is free of malonic ester or alcohol, but sodium malonic ester, as was shown a number of years ago,[1] adds equally well to unsaturated α,β-esters in the absence as in the presence of alcohol. Moreover, according to Nef's views, propyl and isopropyl iodides and sodium malonic ester can give but one and the same product, which should be isopropyl malonic ester, for the addition of reagents whose additive parts consist of hydrogen and an atom or radical negative to that element, invariably leads to an isopropyl derivative. There is, perhaps, no better established fact in organic chemistry than that normal alkyl iodides and sodium malonic ester yield normal alkyl malonic esters, whereas isoalkyl iodides give isoalkyl malonic esters. Furthermore, it is a well known relation that secondary iodides lose hydriodic acid more easily than the primary, and that the tertiary derivatives do so more easily than the secondary; further that it is considerably more difficult to add reagents to alkylenes than to isoalkylenes. If, therefore, the speculations of Nef were permissible, the ease of replacement of sodium in sodium malonic ester should be in the order of tertiary, then secondary, and finally primary alkyl, whereas, even from the earliest investigation on this subject, that of J. Wislicenus, on the replacement of sodium in sodium acetacetic ester by alkyl, it is certain that the relative order of ease of substitution greatly decreases from primary to tertiary iodides; indeed, in this instance, it was found impossible to replace sodium by tertiary butyl.[2] Numerous investigations since then have only emphasized these relations, which in themselves so amply disprove the interpretations of Nef, that any further evidence of their impossibility, which it would be easy to adduce, does not seem necessary.

In the above paper, Nef selected a considerable number of reactions which to him seem abnormal, and as he fails to understand the reason of their apparently abnormal behavior, he

[1] Michael and Schultheiss: J. prakt. Chem., [2], **45**, 55.
[2] Ann. Chem. (Liebig), **212**, 239.
[3] *Ibid.*, 244.

attributed a very mysterious dissociating property to many, comparatively inert, substances, which often, without any apparent reason except to make Nef's views seem less impossible, cause chemical changes involving a great expense of energy. Thus, in regard to the Daimler synthesis, he overlooks the suggestion of that chemist, that the first phase of the reaction consists in the formation of a zinc ethyl derivative, and after reiterating, what Daimler[1] had already emphasized, that the direct formation of zinc malonic ester is practically impossible under these conditions, Nef concludes that his views on the mechanism of this reaction are especially corroborated by Daimler's experiments. The experimental analysis of this reaction mentioned above, shows conclusively that not the slightest support for Nef's views is to be found in the synthesis in question.

Nef's conceptions in regard to the Frankland and Wurtz syntheses are open to the same criticism. Beginning with methyl iodide, the ease of elimination of hydriodic acid increases in the primary alkyl iodides to at least the sixth series; when sodium acts on an iodide it exerts an attraction not only for iodine but also for hydriodic acid, and, if the conditions are such that the formation of hydriodic acid is favored, a correspondingly large proportion of the iodide will pass over into the respective alkylene, which may be more or less reduced by the nascent hydrogen formed by interaction of the acid with the metal used. This formation of alkylene must take place still more easily with secondary and tertiary iodides, in which compounds the capability of direct substitution is decreased, while that of the elimination of hydriodic acid is increased.[2] From this point of view all the facts enumerated by Nef, which he believes to be inexplicable by our present conceptions, are easily explained, and we certainly do not need to take refuge in an hypothesis, that assumes ethylene that will be reduced only to ethyl, because it and hydrogen are formed in the proportion of a molecule to an atom, or whose author[3] particularly emphasizes that, according to his own hypothesis, sodium in reacting on propyl iodide and isopropyl iodide should give the same

[1] Ann. Chem. (Liebig), **249**, 174.
[2] Michael: J. prakt. Chem., **60**, 368–384, 409–424.
[3] Ann. Chem. (Liebig), **298**, 272.

hexane, although he should have been aware that isomeric hydrocarbons have actually been made in this way,[1] and that the physical properties of these two bodies have been carefully examined. The criticism of Nef's views may be left at this point, but it certainly does not seem unreasonable to expect from a chemist, who proposes to revolutionize the present theories, a more thorough knowledge of facts and a better acquaintance with these theories.

TUFTS COLLEGE, MASS.

ON THE FORMATION OF PLATINUM TETRACHLORIDE FROM AQUEOUS HYDROCHLORIC ACID BY ATMOSPHERIC OXIDATION IN CONTACT WITH PLATINUM BLACK.

BY J. W. MALLET.

A considerable quantity of platinum black was prepared from a solution of the tetrachloride, using as reducing agent the commercial solution of formic aldehyde (so-called "formalin") in the presence of sodium hydroxide at the boiling temperature.

The precipitated metal was filtered off, and washed at first with water. When most of the sodium chloride had been washed away the finely divided metal began, as usual, to come through the filter, rendering the filtrate black and turbid. Stopping the washing, the platinum on the filter was allowed to stand for several hours, and had become partially dried when it was attempted to renew the washing with a fairly strong aqueous solution of hydrochloric acid, in the hope that a clear filtrate might be better secured with this than with water alone. Almost immediately the liquid came through the filter clear, but of a deep sherry color, and was found to contain platinum in solution in abundance. Continuing the washing, the color diminished, and after a little while the filtrate was almost as colorless as before turbidity had first appeared in the aqueous washings.

I am not aware that the removal of hydrogen from hydrochloric acid by oxygen occluded from the air in platinum black has been before now observed and recorded.

[1] Schorlemmer: Ann. Chem. (Liebig), **144**, 184; **161**, 277; Bruehl: *Ibid.*, **200**, 184; Zander: *Ibid.*, **214**, 165; Schiff: *Ibid.*, **220**, 87.

NOTES.

Ammonium Amalgam.

Coehn[1] has recently published the results of an investigation on this subject, and these are given here in abstract. The increase in volume which takes place during the formation of ammonium amalgam has been used as an argument in favor of the view that ammonia and hydrogen are absorbed as such by the mercury, and that a distinct substance, ammonium, is not in combination with the mercury. In opposition to this view it has been shown that the volumes of the gases evolved bear to each other the ratio $NH_3 : H = 2 : 1$; and further, that neither ammonia nor hydrogen is absorbed by mercury.

An attempt has been made by Landolt to obtain some experimental evidence of the metallic nature of the substance ammonium, contained in the amalgam, by bringing the freshly prepared amalgam into solutions of salts of the heavy metals and determining whether, under these conditions, ammonium can replace these metals from their salts. Treated in this manner, neither copper, nor silver, nor iron, could be precipitated. This, he says, is opposed to the view that ammonium has a metallic nature.

Le Blanc thought it possible that the ammonium might be so unstable that it would not have the power to replace metals but would decompose into ammonia and hydrogen, as soon as liberated from the amalgam.

He attempted to solve the problem as to the nature of the substance contained in the amalgam by electrolyzing solutions of ammonium salts, using a mercury cathode, and comparing the polarization on the one hand with that which results when an alkali amalgam is formed in this way, and, on the other, with that which is obtained when hydrogen alone is developed on the cathode. If the value found approximates that obtained by electrolyzing an alkali salt it would argue in favor of the existence of ammonium in the amalgam. If, on the contrary, it approached the value when hydrogen alone is developed on the cathode, it would argue against the existence of ammonium. His results pointed to the existence of ammonium in the amalgam.

It has been shown that in addition to the tension at which the development of hydrogen takes place in a reversible manner, as in platinized platinum, there is a characteristic tension for each metal. Thus, the reversible evolution of hydrogen, obtained by discharge of hydrogen on a mercury cathode with

[1] Ztschr. anorg. Chem., **25**, 430.

continuous current, took place at 15.2 volts. If an alkali metal is in solution, using the mercury cathode, there is obtained in addition to the point at 15.2 volts another point beneath this, which changes with the nature of the alkali metal, and is, therefore, characteristic of the latter, and corresponds to the formation of the amalgam. This took pla ce with ammonium at 1.24 volts, and is therefore completely analogous to the case of the alkali metals.

The only argument against the metallic nature of ammonium still remaining was that of Landolt, and it is this which Coehn has tested in a different manner and under different conditions. The ammonium amalgam was freshly prepared by electrolysis and dropped into a solution containing copper sulphate. A platinum wire which was connected through a galvanometer with a platinum plate suspended in the solution projected upward through the bottom of the vessel. The amalgam came in contact with the platinum point, and the action of the element, if copper is replaced, would be to deposit copper on the plate, with the simultaneous passage of a current through the galvanometer. It was found that no copper was deposited, and only a weak current of momentary duration passed through the galvanometer. To test whether Le Blanc was correct in supposing that ammonium was too unstable to replace other metals, he prepared the amalgam so that it would be more stable by electrolysis of ammonium salts, cooled down nearly to 0°.

It was found that the amalgam thus prepared did not show the tendency to swell up unless it was warmed, and it has quite a metallic appearance. When ammonium amalgam, thus prepared, was brought into a solution of copper sulphate, cooled to about the same temperature, the formation of copper amalgam could be seen with the naked eye. Observing these precautions and using the apparatus mentioned above, separation of copper on the plate took place at once.

That the replacement is not due to the hydrogen developed by the decomposition of the ammonium is shown by the fact that metals like cadmium, and especially zinc, which are not reduced by hydrogen, can be precipitated in this way from solutions of their salts.

The author has thus removed the last experimental evidence against the metallic nature of ammonium.

J. C. W. F.

The Density and Molecular Weight of Ozone.

Since Soret's[1] celebrated work on the density and molecular weight of ozone, carried out more than thirty years ago, no

[1] Ann. Chem. (Liebig), 138, 145; and Suppl., V, 148.

work has been done on this subject until Ladenburg[1] took it up in 1898. Soret worked with a mixture of ozone and oxygen containing only 5 per cent of ozone, and hence Ladenburg deemed it important to redetermine these values, using purer ozone.

The ozone which he used was generated in a Siemens' ozonizer, whereby a mixture of ozone and oxygen was obtained containing 8 to 9 per cent of the former, which could be easily liquefied in liquid air. The author liquefied such a mixture by means of liquid air, and then allowed the mixture to boil until most of the oxygen had boiled off. A new mixture of liquid ozone and oxygen was added to the residue, and again the oxygen was allowed to boil off. By repeating this operation several times he succeeded in obtaining 2 to 3 cc. of a blackish-blue, non-transparent liquid. He determined the density of the gas obtained when this liquid was vaporized and also the percentage of ozone in it. The density was determined by measuring the time of escape of the gas from a Schilling's apparatus and comparing it with the time of escape of pure oxygen from the same apparatus. The apparatus had been previously tested with pure oxygen and nitrogen, and was found to give very satisfactory results.

Ladenburg thus found that the gas under investigation required four hundred and thirty seconds to escape, while pure oxygen required three hundred and sixty-seven and four-tenths seconds. Hence, the density of the gas was 1.3698, that of oxygen being 1. The percentage of ozone in the gas was determined by titrating, the iodine liberated from a solution of potassium iodide by a known volume of the gas. It was thus found that the gas contained 86.16 per cent by weight of ozone. From these data the density of pure ozone was calculated to be 1.456, that of oxygen being 1, while theoretically it should be 1.5.

Soon after the publication of these results Ladenburg[2] published a note in which he made a correction. In the calculations by which the above results were obtained, he really assumed the molecular weight of ozone to be 48, while this is what he was trying to prove. So he deduced two algebraic equations, which, when solved, gave him 84.4 per cent by weight as the percentage of ozone in his mixture of ozone and oxygen, and 1.469 as the density of pure ozone.

Shortly after this Staedel[3] and Gröger[4] published, at about the same time, criticisms of Ladenburg's work, in which their chief objection was that it is impossible to calculate the den-

1 Ber. d. chem. Ges., **31**, 2508.
2 *Ibid.*, **31**, 2830.
3 *Ibid.*, **31**, 3143.
4 *Ibid.*, **31**, 3174.

sity of pure ozone when the density of a mixture of oxygen and ozone and the amount of iodine liberated from potassium iodide only are known. Staedel claimed that Ladenburg assumed ozone to be O_3 and that in one of his equations he assumed the action of ozone on potassium iodide to consist in one atom of the oxygen in ozone liberating two atoms of iodine from the potassium iodide, an assumption which he had no right to make, since he was trying to determine whether ozone is O_3. Gröger expressed the belief that it would be possible to determine the density of ozone only when some absorbent was used which would absorb the ozone entirely without leaving behind a volume of oxygen equal to the volume of ozone started with.

In answering these two criticisms Ladenburg[1] agreed with Staedel and Gröger that the molecular weight of ozone cannot be determined from the density of a mixture of ozone and oxygen and the amount of iodine liberated by such a mixture, but he did not agree that this fact detracted from the value of his results.

He again called attention to the fact that the ozone prepared by him was nearly pure. After the oxygen had boiled off at —186° from the liquid mixture of ozone and oxygen, the thermometer rose 60° without any gas being evolved. The determination of the density of his ozone, which contained a little oxygen, gave the value 1.3698, which corresponds to a molecular weight of 43.8. This showed conclusively, Ladenburg thought, that the molecule of ozone is O_3. If, for instance, it were O_4, there would be an error in his results of over 50 per cent, and the conclusion would follow that his ozone contained 60 per cent of oxygen, for which there was not the slightest evidence.

The determination of iodine liberated from potassium iodide was made merely to ascertain the percentage of ozone in his mixture, which was found to be 84.4 per cent. This value was then used in correcting the density found to that of pure ozone and 1.469 was the result obtained, which corresponds to a molecular weight of 47.

Quite recently Brunck,[2] in an article on the quantitative determination of ozone, referred again to the apparently inadequate proof of Ladenburg that ozone has the molecular weight 48. This reference called forth another reply from Ladenburg,[3] in which he used substantially the same argument which he used against Staedel and Gröger, and further he criticizes some of the results of Brunck regarding the liberation of iodine from potassium iodide in acid solution. Brunck[4] answered these criticisms in a later paper. C. E. C.

[1] Ber. d. chem. Ges., **32**, 221.
[2] *Ibid.*, **33**, 1832.
[3] *Ibid.*, **33**, 2282.
[4] *Ibid.*, **33**, 2999.

The Lavoisier Statue in Paris.

On the 27th of July, 1900, a bronze statue of Lavoisier, erected on the Place de la Madeleine, where the residence formerly occupied by him stands, was unveiled in Paris. The statue was designed by Barrias and was purchased with contributions from scientists in all parts of the world. As Moissan said, in presenting the statue to the city: "The master sculptor Barrias has recalled him to us in all the lustre of his power and intelligence. With raised head and extended chest he appers to be answering his detractors and defending his famous theory of combustion." On the pedestal are two high reliefs, one representing him in his laboratory, dictating to his wife the results of his experiments, the other picturing him in the Academy of Sciences explaining to his students his work and his theories. The principal address was made by Berthelot, whose remarks regarding the work of Lavoisier should receive more general notice. On the basis of the great discoveries which have done so much to enrich the world, to improve the industries, and to advance the intellectual and material condition of its inhabitants he regards Lavoisier as worthy of being classed with Galileo, Newton, and Leibnitz. He says: "Lavoisier has merited the esteem of men, from the philosophical point of view, because he has established the fundamental laws which govern chemical transformations of matter; from the practical point of view, because these laws have become the foundation stone of the innumerable industries based on these transformations. Lavoisier is one of the great benefactors of humanity." He refers to the discovery of the fundamental fact, upon which all the others are based as "that of the chemical constitution of matter and the distinction between ponderable bodies and imponderable ones, as heat, light, and electricity, to whose influence the ponderable ones are exposed. The discovery of this distinction overthrew the old conception of the four elements, corresponding to the four physical states of matter, earth, fire, water, and air, elements which combined in different proportions and according to different laws, to produce all substances known, and to transform one into another." * * "An error not less important than that of transmutation was that of the variability in the weight of bodies exposed to the action of heat, a variation apparently verified by common experience and observation." * * "It is often said that the use of the balance dates only from the last century; but this is an error, as it had been used for centuries and even appeared on the monuments of ancient Egypt." Lavoisier used it to confirm his interpretations of the chemical nature of the act of

combustion. "Two causes had tended to delay the true explanation of the facts; the slight knowledge concerning the weights of different gases and the methods of distinguishing one from another, and ignorance regarding the composition of air and water, until then supposed to be undecomposable elements." Lavoisier alone, it is true, did not furnish the evidence necessary to establish the composition of air and water; but profiting by the work of his predecessors and contemporaries he realized the conditions underlying the actions, and was enabled to demonstrate the laws and give the true interpretation. The two great questions, therefore, which Lavoisier settled were, first, what had never before been proved, the distinction between ponderable and imponderable bodies, and, second, the nature of combustion, showing the quantitative relationship between the weights of a gas and a body heated in the gas, and the weight of the final product. These observations led to further experiments and to important deductions regarding the composition of acids and metallic oxides, the composition of air and water, that of organic matter, and the rôle which heat plays in chemical action and in the animal body and the nature of respiration. The observations of Priestley and Black, regarding the necessity of oxygen for respiration and the formation of fixed air, had no apparent connection until Lavoisier applied his combustion theory to the phenomena of respiration and showed the complete analogy between combustion and respiration and the importance of the heat of combustion to the animal body. After referring to other discoveries which were the natural consequences of Lavoisier's work, Berthelot says: "I do not claim that Lavoisier was the personal and direct author of all the discoveries which I have enumerated; but it is certain that he was the one who established the solid foundation upon which the edifice of modern chemistry has been built and without which the discoveries would not have been made." In closing he quotes some remarks of Lavoisier's: "It is not absolutely necessary, in order to merit the esteem of his fellow men and to fulfil his duty to his country, that one should take part in the administration and regeneration of empires. The scientific worker is able, in the quiet of his laboratory, to perform patriotic deeds; he aspires by his work to diminish the suffering of the human race and increase its possessions and happiness and thus to deserve the glorious title of benefactor of the human race."

J. E. G.

AUSGEWÄHLTE METHODEN DER ANALYTISCHEN CHEMIE. Von PROF. A. CLASSEN. Erster Band. Braunschweig: Friedrich Vieweg u. Sohn. 1901. xx + 940 pp.

The general plan of this book is much the same as that of Sir William Crookes' "Select Methods in Chemical Analysis," from which too a considerable part of the matter has been taken. The work is intended mainly for technical chemists and advanced students, so that it assumes a general knowledge on the part of the reader of the commonly employed analytical processes. Special attention is given to the rarer elements, some of which, as for example thorium, have acquired industrial importance of late years. Electrolytic methods for the determination and separation of the metals to which such methods are applicable receive also prominent notice, as might be expected from the long-continued investigations of the author in this direction.

The scope of the book is confined to inorganic chemistry, but, as the title-page gives notice that this is only the first volume, it may be supposed, without any special promise, that hereafter the methods applicable to organic substances will be considered. Some excellent processes are omitted, as for instance the separation by means of amyl alcohol of lithium chloride from the chlorides of sodium and potassium. On the other hand, some of the analytical methods for the examination of industrial products are quite interesting—such as those for the examination of the different kinds of glass, and some of the features of iron and steel analysis as practiced in Germany, which differ from those in general use in America.

The printing and the illustrations are very clear and good.

J. W. M.

THE CHEMICAL ANALYSIS OF IRON. A complete account of all the best known methods for the analysis of iron, steel, pig-iron, iron ore, limestone, slag, clay, sand, coal, coke, and furnace-producer gases. By ANDREW ALEXANDER BLAIR. Fourth edition. Philadelphia and London: J. B. Lippincott Co. 1901.

The fourth edition of Blair's "Chemical Analysis of Iron" appeared in its usual attractive form. The author has wisely decided in this edition to avoid the use of symbols and formulæ in the text, and to adopt a uniformly consistent modern nomenclature. This has necessitated a complete rewriting of the book, which has gained thereby also in minor changes that have been made in arrangement and statement.

This edition preserves the general character of the former ones. No attempt has been made to bring before the busy

"iron" chemist the immense number of new processes which appear from year to year in this field of chemical research. To some this will be a matter of regret, while to others the author's restraint will be commended. For, as has been said in notices of previous editions of this work, the book is mainly characterized by being a record of the personal experience and original work of a chemist of strong individuality.

New and valuable matter has indeed been added, notably the method for the determination of phosphorus prepared by the subcommittee of the International Steel Standard Committee of the United States; and the methods for the analysis of coal and coke from the Report of the Committee on Coal Analysis to the American Chemical Society.

A criticism may perhaps be fairly made (although it may possibly seem trivial) on the retention in many places of the subheading "Rapid Methods." The classification of chemical processes on the basis of the time required for their performance is a relic of the day when iron chemists were compelled to hurry their work to satisfy the unreasonable demands of furnace men, and a rapid process was then often synonymous with a hastened process not pretending to the highest accuracy. Now-a-days, however, many of the rapid processes surpass in accuracy the slower ones which they have replaced. In the whole history of analytical chemistry there is nothing more interesting and instructive than the development of the process for the determination of phosphorus whereby results can be obtained in less than an hour which formerly took days, results, too, which in uniformity and accuracy leave nothing to be desired.

This work of Mr. Blair has stood the test of time and remains the first authority in the field of chemical analysis of iron, a model in its clearness of statement and completeness of information.

T. M. Drown.